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Journal
of
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Devoted to Science and the Mechanic Arts

Vol. 224 SEPTEMBER, 1937 No. 3

POLAROID AND THE HEADLIGHT PROBLEM.*

BY

EDWIN H. LAND,

Land-Wheelwright Laboratories, Boston, Mass.

For more than twenty years most physicists and illuminating engineers have realized that the ideal solution of the headlight glare problem lies in the use of polarized light; and the list of names of men who have concerned themselves with this problem is an imposing selection of leaders in science. This interest is manifested by the grant of patents a decade or more ago to many scientists in many countries.

In view of the eminent position of the scientists who have for so long recognized the merits of polarized light as a solution of the headlight glare problem, why has polarized light never been used on automobiles?

The answer is simply that no polarizer whatsoever has been available suitable for automobile use.

To make this clear, let us review rapidly the nature of polarized light and the history of the only polarizers which have been known until recently.

As you all know, modern physics is largely concerned with the conflict in the relationship between two theories—the theory that light is a stream of bullet-like particles, and the theory that light is a wave motion. The very simple problems

* Presented at a meeting held Thursday, November 5, 1936.

(Note—The Franklin Institute is not responsible for the statements and opinions advanced by contributors to the JOURNAL.)

of polarization that will be discussed tonight require only the wave theory. You should have clear in your mind, however, the explanation of why light can be polarized while sound cannot. Fig. 1 shows a sound wave, diagrammatically, coming from the bugle; the arrows parallel to the direction

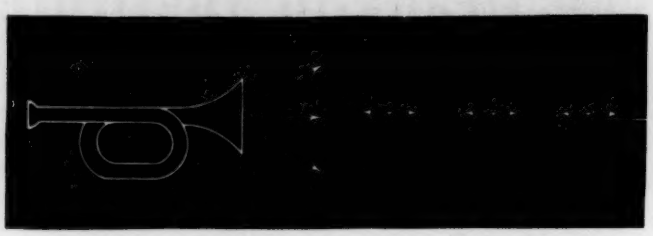

FIG. 1.

of the sound are supposed to indicate that the vibration of the medium—air in this case—is in the direction of the line of propagation of the wave of sound. There are a great many experiments which prove that this kind of vibration occurs in the transmission of sound.

Nobody knows what happens in light. Although Fig. 2, which is taken from a standard text, shows arrows at right angles to the line the light is following, there is absolutely no experimental proof that this condition exists.

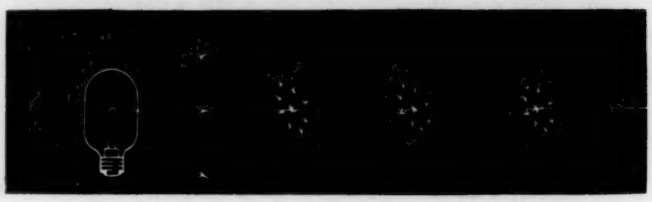

FIG. 2.

When light engages in a one-sided activity, such as striking a table top at an angle or traveling through a crystal in which the atoms are related to one another in a nonsymmetrical way, it emerges from this activity with more or less one-sided or nonsymmetrical properties of its own. The next time it engages in any activity it will behave differently. Its

behavior depends on the relations between the newly-acquired asymmetry of the light ray and any asymmetry in the new engagement. Fig. 2 shows the light ray with arrows at right angles to the direction of the travel of the ray. The correct way would be to have question marks along the ray up to the place of its first asymmetrical activity, such as striking the table top or, as we shall see later on, striking a polarizer. The arrows, however, can be considered as indicators of the symmetry which can usually be assumed to exist in most of the light from an ordinary incandescent source, such as a coil filament in an ordinary electric light bulb, or the sun. Similarly, we could use the arrows to indicate asymmetry introduced by an asymmetrical event. The word asymmetrical is used here in a special sense of nonuniform. Now the only way in which we can imagine this nonuniformity is to conceive of a wave motion much different from that of the sound wave. We must imagine a light ray in which the displacement of whatever it is that is displaced is not along the line of the ray but at right angles to it.

I have tried deliberately and precisely to bring you to a state of confusion, because this will be an accurate representation of present understanding of this phenomenon.

The usual thing is to make all clear with a piece of rope. The rope analogy is so simple that it gives a sense of comfort and understanding.

Fig. 3 shows the rope trick. The lecturer vibrates the rope, sending waves down its length. The rope passes through a picket fence and then through another picket fence and then through a gate with its pickets running horizontally. The idea is that between the lecturer and the first picket fence the waves, although moving along the rope, are pushing along sideways in all directions—that is, they are transverse vibrations. The vertical part of each wave gets through the first picket fence so that between the two picket fences all the waves lie in a vertical plane. Clearly, these waves will go right through the second picket fence and continue on to the gate, but the gate is closed to them because the slots in the gate are horizontal, and vertical waves have no horizontal component. In this analogy we are interested only in the waves, not in the rope, so you must ignore the part of the rope between the gate and the tree where no waves travel.

As we said earlier, we actually know nothing about the wave between the lecturer and the first picket fence except that it behaves symmetrically. From the way the second fence does *not* affect the wave and from the way the gate *does* affect it we can deduce that the first fence is a linear experience or, in our special sense of the word, an asymmetrical experience for the light.

Of course the picket fences and the gate represent polarizers, the two picket fences being parallel polarizers, the gate being a polarizer crossed with the others.

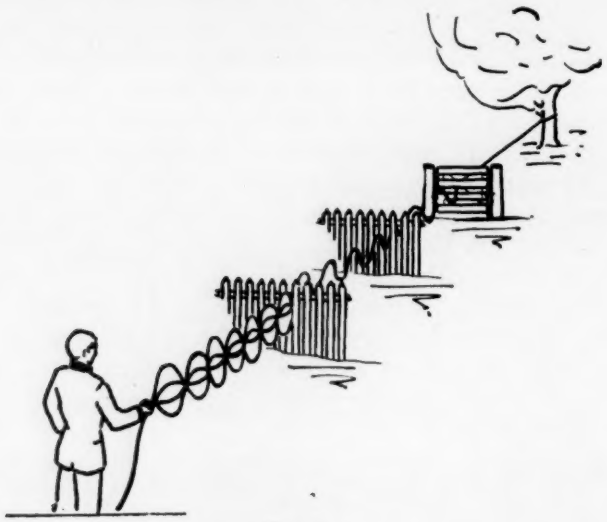

FIG. 3.

Let us now compare the action of Polaroid discs, as a light ray travels through them, with our rope analogy to see how the analogy explains the action of the Polaroid and also to see how the action of the Polaroid explains the analogy. Here we have a projector. The light ray travels from it to the first Polaroid, from there to the second Polaroid and on to the third which blocks it. (In order to give you a direct view of the action of crossed polarizers, let me hold these two discs first parallel and then crossed.) As you can see, the light waves between the projector and the first Polaroid reveal nothing of their nature, nor do they between the first

Polaroid and the second, except that a light meter would show that while the intensity fell by one-half after traversing the first Polaroid the intensity decreased no further upon traversing the second. When the light strikes the third polarizer, however, which is just like the other two but crossed with them, there is dramatic evidence that something unusual has happened to the light. The peculiar inter-relation of the behavior of these three polarizers has been explained by assuming that whatever the light was before it hit the first Polaroid it was at least symmetrical, for although the first Polaroid absorbs half the light, it absorbs no more and no less than half no matter how we turn it; by assuming further that light after it has passed the first Polaroid is no longer symmetrical, because the light transmitted by the second polarizer *does* depend upon how it is turned in relation to the ray; by assuming, in short, a similarity between the optical action of the Polaroids on the light ray and the mechanical action of the pickets upon the rope waves.

What far-sighted physicists appreciated twenty years ago about the problem of headlight glare was that if the headlight lenses and windshields could be made of optical "picket fences," with the pickets parallel to each other and at, for example, 45° to the road, the headlight problem would be solved. For it is apparent that each driver would see his own light as it illuminated the road, because the rays reflected by objects illuminated by his headlights would pass through his windshield; whereas his windshield would have its optical slots crossed with those of an approaching headlight.

The principle was plain. The problem was to find the optical picket fence.

There is not time tonight to review the development of the knowledge of polarized light—one of the most elegant chapters in the history of physics. But we can review the history of the devices used to make polarized light.

In 1670 Bartholinus placed a rhomb of calcite on some writing and saw the writing doubled. He did not know it, but the twinned line was polarized. Huygens later placed another rhomb of calcite on top of Bartholinus', found he could twin the twin, and came to the conclusion that the light

in passing through the first rhomb had lost a characteristic which it had had before. But Bartholinus could not have used the knowledge, even if he had had the problem of headlights in his day, because he would have needed rhombs of precious calcite as big as a whole automobile.

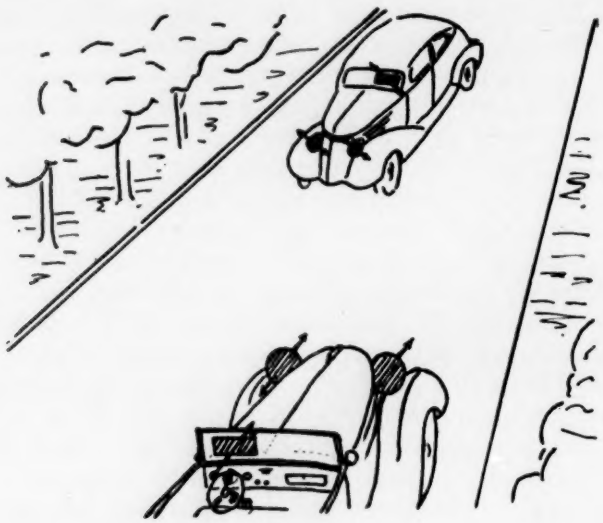

FIG. 4.

Malus in 1808 had the enviable experience of looking across the garden through a calcite rhomb to the windows of the Luxembourg Palace glaring in the afternoon sun, and finding that in one of the two images which he saw, the brilliant image of the sun was extinguished. It is proper to regard this experiment as the first use of a polarizer for the elimination of glare. For at least two reasons the experiment could not be transferred to automobiles: first, because, while the asymmetrical impact of a ray of light as it strikes glass at an angle does polarize it, only some 10 per cent of the light is reflected and the transmitted 90 per cent has too little polarized light in it; second, the calcite rhomb obviously cannot be used for a windshield.

Arago in 1812 used a pile of plates to intensify the effect that Malus had first observed and obtained an appreciable

degree of polarization in both the transmitted and the reflected rays. If glass were perfectly transparent and if we could use an infinite number of plates or even a few dozen, we would have a polarizer. But glass is far from perfectly transparent. The plates must be placed at an angle and the windshield would suffer from such entirely unacceptable defects as the displacement of the image by the huge pile of plates, a cloud of multiple reflections, and the hazard of a hundred unlaminated sheets before the eyes.

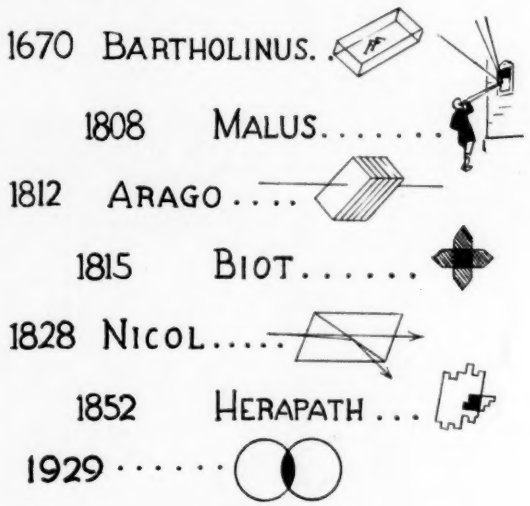

FIG. 5.

Biot in 1815 discovered another polarizer—tourmaline—a semi-precious gem, a rather thin sheet of which polarizes light by simple transmission. Needless to say, we can dismiss this polarizer as a possibility for automobile use, because of its high cost and because, to quote Preston, "Tourmaline is not a very transparent mineral, and strong beams of polarized light cannot very well be obtained with it. Hence, it is quite unfitted for work where the illumination is faint."

Nicol in 1828 devised an amazingly ingenious way to divert from the field of view one of the polarized beams which Bartholinus had seen when he looked at the twin images through

calcite. The Nicol prism gives a pure polarized uncolored beam, but it still involves the use of large rhombs of calcite which, because of their rarity, are extremely high in price. The world supply is limited. There are hardly enough of the natural crystals to cover the headlights of the cars of a single city block. Cutting the calcite in the way that Nicol prescribed requires great skill and the finished prisms are susceptible to temperature changes and to shock. Because of their limited angular aperture they cannot be used in a windshield, for it would be impossible to see anything that was not straight ahead. At current prices Nicol prisms for a single headlight, if they could be collected, would cost a hundred times as much as all the rest of the car. Clearly, the Nicol prism, excellent in its way, is for commercial and technical reasons impracticable for automobile use.

In 1852 Dr. William Bird Herapath discovered in his microscope the remarkable polarizing property of the tiny crystals that form upon combining iodine with quinine salt. These tiny crystals inspired him to a mighty enthusiasm which flowered into a series of articles in the *Philosophical Magazine*, each article describing another attempt to convert these minute microscopic crystals into sizeable areas—and sizeable meant to him an area large enough to cover a microscope eyepiece 1/8″ in diameter. Herapath failed.

Professor Cheshire, in his 1923 presidential address to the Royal Microscopic Society, earnestly urged concentrated research on the problem of making a microscope polarizer and said regretfully of Herapathite, "Promising as they were, these artificial tourmalines have not stood the test of time."

But though Herapath failed to produce a material in useful form, his vision of what he hoped to accomplish, his enthusiastic and eloquent descriptions of what he thought he was just about to achieve, have been a vital stimulus to all who have in the last eighty years encountered his writings. Herapath did not discover the material, only its polarizing properties. But he took the new polarizer to his heart with the same elation that subsequent readers throughout these eighty years have felt over the material. He felt that it was his very own, even as each successive generation of readers

have felt that in discovering his articles they have discovered his polarizer. I confess that no one felt this proprietary interest more keenly than I did upon my first reading of his articles. The old Ganot's *Physics* mentioned Herapathite, but modern physics books do not. Old editions of the Encyclopedia Britannica mentioned Herapath, but you will not find his name in the last edition. Webster's Unabridged Dictionary does not seem to mention Herapathite, but you will find it, in small print under "obsolete words." Beneath the surface of current optical information it is just hard enough to find to give each searcher a thrill of discovery.

No sooner had I read of Herapathite than I set out to apply it to automobiles. No doubt many before, and certainly many since, have done the same. What did it matter that these crystals grew so small? What did it matter that in seventy years following Herapath's complete failure to produce an area of usable size not a single paper appeared describing any success in improving the unsuccessful process? In spite of Herapath's admission that the fragile crystals fly apart when touched with blotting paper, one could with what one vaguely thought of as modern methods succeed where he had failed, grow large areas, or piece small areas together to render polarizing the windshields and the headlights of our cars. In a secret sort of way this feeling was abroad probably long before my time. Professor Robert W. Wood, our American authority on physical optics, tells the story of a letter he received from the research laboratory of a large automobile company: "Can you prepare an extensive area of Herapathite?" Professor Wood replied, "I am extremely sorry to inform you that I do not know how to make a polarizing windshield."

It is a curious property of research activity that after a problem has been solved the solution usually seems obvious. This is true not only for those who have not previously been acquainted with the problem, but also for those who have worked over it for years. As they regard their finished work they cannot help wondering why a simple, rational process that can be performed in a day took them, rational people, ten years to develop. In research, as in the whole civilizing process, why does it take so long to learn so little? In our

laboratory notebooks, as we review them, it is as hard to find the answer to research slowness as it is difficult to find the answer to civilizing slowness in our history books. There is the same strange interpenetration of methodical, intellectual activity stimulated and interrupted by irrelevant emotional and economic daily problems.

The process that is now being performed every day in the manufacture of Polaroid took some ten years to develop. It derived by antithesis from Dr. Herapath's valiant efforts. His efforts and the efforts of his successors over some seventy years failed because it was hard to get the fragile crystals to grow over large areas.

The opposite procedure of using extremely small crystals is the solution.

Some of the problems encountered in using these small crystals may be of interest. If these small crystals are to be used, their polarizing axes must all be turned the same way in uniform orientation. Plainly they must overlap to cover the whole area. It would not be clear beforehand whether a binder were necessary for holding the crystals in place, nor would it be clear how they would be turned into uniform orientation, nor would it be obvious just how small the crystals should be.

Let us consider first the problem of uniform orientation. It is apparent that all these crystals must be placed in a field of force and the only conceivable fields of force are the electric, magnetic, gravitational, and mechanical. How was the choice to be made?

How much should the crystals overlap?

If a binder is necessary, is there one which will not destroy the crystals mixed with it? Should it be a binder at all or should it be a self-supporting sheet-like matrix for the suspended crystals?

What shape should the crystals have?

The difficult and exciting thing about this type of research is that the answers to almost all of these questions are interrelated and have to be given together. The shape of the particles depends upon how they are going to be turned, and the way they are going to be turned depends upon the matrix which is to be selected. The way in which they are to be

turned depends upon the size of the particles, and the size depends upon how much is to be overlapped, which depends in turn upon the polarizing power of the crystals, and the polarizing power of the individual crystal depends upon its thickness. A further confusing factor is that many choices will give a degree of success. A great number of successful combinations have been employed in the history of the development of Polaroid. What choice did we finally make and how did we arrive at it?

Here is a piece of Polaroid sheeting. It is, as you see, flexible and tough, strong, not inflammable. It is perfectly stable, because it answers the matrix question by employing cellulose acetate. The polarization is uniform over the whole area and the sheet is clear to look through because the size selected for the crystal is smaller in one dimension than the wave-length of light. The sheet, as you see, is unlimited in area because a mechanical process allows continuous production. And the sheeting is cheap—cheap enough for automobiles because this mechanical process is rapid and substantially automatic and the raw material low in cost.

These satisfactorily related choices of process are the result of a handful of sound perceptions isolated from thousands of groping approaches. There was a time when it seemed as though the work were done. We had a good polarizer, made by what seemed a good process, but the first road test proved that the crystals, small as they were, were far too large for windshield use. The windshield lighted up like a ground glass when illuminated by the approaching light. The already microscopically small crystals had to be many times smaller, so small that they could not be seen even in a high-powered microscope. This presented an interesting dilemma since these tiny crystals had to be by definition invisible individually. The only way of finding out whether or not they were polarizing crystals was to orient them, but it was far from sure that our orienting technique worked with such small crystals and we could not test for orientation without knowing that we had polarizing crystals. A mass containing unoriented polarizing particles is blackish and opaque, since the little individual polarizers are crossed with one another. When the crystals are oriented, the mass should

become white and transparent. If, in our efforts to make these very small crystals, the mass had failed to become transparent we could not have told whether the orienting technique was failing because the crystals were so small or whether the crystals were simply opaque and nonpolarizing.

Now I should like to have you actually see one way of making one form of Polaroid. In order for you to appreciate the fascinating geometry of this process, please let me call your attention to this slide which describes how the random orientation of a mass of suspended crystals is converted to a uniform orientation by stretching the mass. Imagine a sheet of rubber held between the hands and a pencil lying at an angle to the direction of stretch. As the stretch is increased, the pencil will turn parallel to the direction of stretch, approaching perfect parallelism as a limit as the stretch is continued. Looking now at the graph, note the line at 45 degrees indicating the average orientation of completely random crystals. The length of the radial lines is proportional to the stretch, and the angles at which they lie respectively indicate how the mean angle of all the crystals has shifted towards the direction of stretch as the stretch increases. You see that for a stretch of one hundred times, the crystals cluster closely around the direction of stretch.

Now I shall let you see what happens when we perform this process. (Stretching of opaque mass of Herapathite crystals suspended in an elastic medium; beginning of light transmission, increasing to substantial transparency; extinction of the light by a polarizer crossed with the axis of the newly-made polarizer.)

The Polaroid which is now being made in quantity for industrial and scientific uses, and the material which will be used in automobiles, is made by a process, the principle of which is not unlike that you have just witnessed.

CLASSIFICATION OF THE APPLICATIONS OF POLAROID

I. *Utilization of Natural Polarization*
   1. Reading Lamps
   2. Sun Glasses
   3. Filters for Visual Instruments
   4. Photography
   5. Display illumination

II. *Use of Extinction of Light by "Crossed" Polaroids*
1. Headlight Glare Elimination
2. Adjustable Sun Glasses
3. Photometry
4. Optical Activity
5. Light Valves

III. *Use of Interference of Polarized Light*
1. Colored Illumination and Flood-lighting
2. Advertising Displays
3. Polarizing Microscopes
4. Strain Testers for Transparent Products and Models

IV. *Discrimination Between Specular and Diffuse Reflection*
1. Photography
2. Reading Lamps
3. Inspection of Surface Textures and of Pigments

V. *Use in Binocular Vision*
1. Stereoscopic Viewing Devices
2. Stereoscopic Movies
3. Binocular Ophthalmic Instruments
4. Binocular Studies in Experimental Psychology

Honeycomb Metal Wing Features New Wight Passenger Airplane.—W. F. SHERMAN. (*Iron Age*, Vol. 140, No. 1.) Working inside the limited space of an airplane wing, Barkley-Grow Aircraft Corp., of Detroit, has fabricated an all metal honeycomb structure of great strength and lightness to support its new eight-passenger, bi-motored metal plane. Departures from conventional practice in aircraft wing structural design have made possible a great simplification in stampings, riveting, assembly and finally in putting on the metal covering of the wings. New rivet "squeezing" equipment has been devised and built to take advantage of this possibility of easy and rapid construction. Because of this new wing's adaptability to mass production at low cost and its invulnerability to gun-fire and shrapnel, it has aroused the interest both of commercial and military aviation groups. The wing has neither conventional spars (beams) nor ribs (fore and aft formers). Instead it is built up of a series of rectangular tubes, or cells, which provide the equivalent of eight spars. Construction consists of the assembly of a number of spanwise webs of thin sheet aluminum alloy, flanged for assembly purposes, and lightened by means of punched, flanged holes. Bottom and top covering, Alclad sheet, is riveted to the internal structure. This arrangement produces 27 uniformly tapered tubes or cells extending outward to the wing tip. Fully cantilever, this wing structure has no supports outside in the airstream, all bending, drag and torque loads being carried by the internal structure and metal covering.

R. H. O.

THE ENERGY HUMP IN CHEMISTRY. I.

BY

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INTRODUCTION.

There are a great many reduction-oxidation systems which do not fit into the orthodox picture. Potassium nitrate and nitrobenzene are readily reduced; but neither one gives an oxidizing potential with a platinum electrode. Alcohols and many other organic compounds are readily oxidized; but give no reducing potentials. An overwhelming majority of organic compounds cannot be rated electromotively as oxidizing or reducing agents, although they can be reduced or oxidized at fairly definite potentials. Even here there are discrepancies. Dimethyl acrylic acid can be reduced readily in acid solution at a platinum cathode but not by a chromous chloride solution which is approximately 0.4 volt less noble than the platinum cathode. Sulphurous acid and sodium sulphite can be oxidized electrolytically without any difficulty; but aqueous sodium sulphate cannot be reduced under any experimental conditions that have yet been realized. Concentrated sulphuric acid was reduced electrolytically by Faraday; but ordinary solutions of sulphuric acid cannot be reduced electrolytically.

Metallic oxides, such as those of manganese, are stronger oxidizing agents and less stable thermally the more oxygen they contain. No such relation holds for potassium hypochlorite, chlorite, chlorate and perchlorate. The thermal decomposition of potassium chlorate into chloride and oxygen has never been reversed experimentally, indicating that potassium chlorate is a metastable compound; and yet there is no experimental evidence that either potassium chlorate or perchlorate will revert to chloride to any appreciable extent in any reasonable time. While a potassium chlorate solution can be boiled with hydrazine without any reduction taking

place, the presence of pulverulent copper causes quantitative reduction apparently at ordinary temperatures.

All these difficulties and many others disappear if one introduces, at first as a working hypothesis, the concept of the energy hump. We postulate that systems exist which will not react unless some of the molecules of one or more of the substances, which should react from the free energy relations, are raised to an energy level or to energy levels higher than those reached by any of the molecules under ordinary conditions. In the case of the energy of activation it is assumed that relatively few molecules reach the reactive energy levels under ordinary conditions. As stated, we are assuming that in certain systems none of the molecules reach the reacting energy levels under ordinary conditions. The concept of the energy hump is, therefore, the concept of the energy of activation carried to its logical conclusion. From the experimental behavior of systems in which we postulate the occurrence of energy humps, we deduce that the energy hump tends to disappear with increasing concentration, rising temperature, and the presence of suitable catalytic agents. When a reaction can be made to take place electrolytically, the energy hump is defined as the difference between the free energy and the voltage necessary to produce the reaction.

The concept of the energy hump as we are developing it is new to everybody and has not yet been received with enthusiasm by anybody to whom it has been presented. It carries with it the corollary that certain reactions which are permitted by the free energy relations will not take place to any extent even in infinite time. In other words, it postulates a zero reaction velocity in certain cases, whereas all other physical chemists postulate nowadays a finite, though often incredibly small, reaction velocity. On the other hand, if we are right it means that the physical chemists can deal with organic chemistry as a whole instead of being limited to special chapters as at present. Of course the concept of the energy hump is not limited to reduction-oxidation reactions. They are, however, the best systems with which to start, because we can determine certain chemical potentials by means of electromotive force measurements.

The question at issue is not whether the concept of the energy hump is right or wrong; but whether it is a helpful working hypothesis We shall now present a few of the reasons that make us believe that the concept satisfies this criterion.

ELECTROMOTIVE FORCES.

When electrolyzing a solution, the products set free at the electrodes are those requiring the lowest voltage under the conditions of the experiment. Consequently, we know that other products which might have appeared require a higher voltage to produce them. When we charge a storage battery and convert lead sulphate into lead peroxide, we know that it takes a higher voltage to set free oxygen; that conclusion is verified experimentally when we reach the end of the charging period. If we electrolyze aqueous caustic soda, we get hydrogen at the cathode and we conclude that the discharge of sodium ions require a higher voltage. We can check this experimentally by lowering the voltage at which sodium ions discharge. With a mercury cathode we get primary discharge of sodium ions and the formation of sodium amalgam. That is elementary now; but people opposed bitterly the concept of primary decomposition of water when it was introduced by LeBlanc forty-five years ago.

When we electrolyze dilute sulphuric acid, we get hydrogen at the cathode and we conclude that the voltage necessary to reduce sulphuric acid to sulphurous acid is higher than that necessary to set free hydrogen. We can check this experimentally by increasing the concentration of sulphuric acid and by raising the temperature, in which case we get reduction to sulphurous acid and then to hydrogen sulphide.[1] If we raise the voltage necessary to set free hydrogen, by using a zinc or mercury cathode, we can reduce sulphuric acid at a somewhat lower concentration or at a somewhat lower temperature.

A sulphur dioxide electrode [2] in molar sulphuric acid is roughly 0.4 volt more noble than a hydrogen electrode. At ordinary concentrations and temperatures a cathode over-

[1] Bancroft and Magoffin, *J. Am. Chem. Soc.*, **57**, 2561 (1935).

[2] Lewis, Randall and Bichowsky, *J. Am. Chem. Soc.*, **40**, 356 (1918).

voltage of one volt is not sufficient to reduce sulphuric acid. Consequently, to pass electrolytically from $H_2SO_4 + H_2$ to $H_2SO_3 + H_2O$ in molar solution means passing through an energy level at least 1.4 volts higher than the final level. Nobody has determined whether a sulphur dioxide electrode in concentrated sulphuric acid is strictly reversible or not. Assuming it to be reversible or nearly so, the energy hump for aqueous sulphuric acid can be varied, by changing the concentration, from approximately zero to a value which is certainly not less than two volts and may be a good deal more. We have no method at present for determining the theoretical voltage necessary to reduce dilute sulphuric acid. One could make determinations at a zinc or mercury cathode with fairly concentrated sulphuric acid solutions and then plot the observed figures against the concentrations; but the extrapolation would probably be so excessive even at 100° as to make the result worthless.

People have become so used to speaking of electromotive forces of reversible reactions that most physical chemists believe that an irreversible reaction cannot give a definite electromotive force. This is wrong both theoretically and experimentally. A given solution of sodium sulphite is at a definite energy level and changes to another energy level when it is oxidized to sodium sulphate. Since this change can be made to take place electrolytically under practically constant conditions, it must and does give a definite electromotive force. Schaum, G. N. Lewis and A. A. Noyes have each studied the sulphite-sulphate electrode and have had no difficulty in getting measurements which they were willing to publish. Dry cells are not reversible but hundreds of millions of them are sold.

We have shown [3] elsewhere that, at constant temperature and constant pH, the potential difference at a sulphite-sulphate electrode should be a function of the concentration of the sulphite and independent of the concentration of the sulphate as a reaction product. Schaum [4] and von der Linde [5] found that the electromotive force of a sodium sul-

[3] Bancroft and Magoffin, *J. Am. Chem. Soc.*, **57**, 2561 (1935); **58**, 2187 (1936).
[4] Schaum, *Z. Elektrochemie*, **7**, 483 (1901).
[5] Von der Linde, Inaugural Dissertation, Marburg (1902).

phite-sulphate electrode varies with the concentration of the sulphite as it should, and that it makes no difference whether one dilutes with water or with sodium sulphate. Lewis, Randall and Bichowsky [6] found that at constant temperature and constant pH the change of electromotive force with change of concentration of sulphurous acid was described very well by the theoretical formula. They did not find that the sulphate concentration had no effect; but that was because they varied the pH at the same time. This gap was filled by Noyes and Steinour [7] who showed that when the hydrogen-ion concentration is nearly the same, addition of hydrochloric acid or of sulphuric acid to a sulphurous acid electrode gives substantially the same electromotive force. We have shown that adding sodium sulphate to a sodium sulphite electrode gave a slight increase in electromotive force instead of a decrease.

Although cystine can be reduced to cysteine by tin and hydrochloric acid, the reduction apparently does not take place reversibly because the electromotive force of a cysteine electrode varies with the concentration of cysteine as it should and is independent of the cystine concentration.[8] Michaelis and Flexner report, p. 721, that "a solution of cysteine in absence of oxygen establishes a definite potential at an indifferent non-attackable electrode. This potential is independent of the concentration of cystine and depends logarithmically on the concentration of cysteine [over the range from 0.1 M to 0.002 M at a pH of 4.6] and of hydrogen ions. The potential is identical at electrodes of blank platinum, gold-plated platinum, and mercury, and reproducible to within five millivolts. Slight traces of oxygen displace the potential to the positive side. Mercury is much less sensitive to oxygen than platinum or gold-plated platinum and has the advantage of yielding final values in a relatively short time."

The question whether a given substance, which can be oxidized or reduced, will function as a reduction or an oxida-

[6] Lewis, Randall and Bichowsky, *J. Am. Chem. Soc.*, **40**, 356 (1918).

[7] Noyes and Steinour, *J. Am. Chem. Soc.*, **51**, 1418 (1929).

[8] Dixon and Quastel, *J. Chem. Soc.*, **123**, 2943 (1923); Dixon, *Proc. Roy. Soc.*, 101 B, 57 (1927); Michaelis and Flexner, *J. Biol. Chem.*, **79**, 689 (1928).

tion electrode is a simple one from our point of view.[9] If a substance does not pass through a more strongly reducing stage while being oxidized, it will give an electromotive force with a non-attackable electrode quite apart from any catalytic action of the electrode or of the solution. If the substance does pass through a more strongly reducing stage while being oxidized, it will not act electromotively as a reduction electrode unless the electrode metal or the solution is a sufficiently powerful catalytic agent to eliminate the effect of the energy hump. The converse is true for an oxidizing agent.

Any given reduction-oxidation system may be reversible both ways as with the ferrous-ferric electrode; it may be reversible one way as with the cysteine-cystine electrode; or it may be irreversible both ways as with the chloride-chlorate or chlorate-perchlorate electrode.

The concept of the energy hump accounts for potassium nitrate, nitrobenzene, and acetic acid not giving oxidation potentials, and for ammonia, aniline and alcohol not giving reduction potentials. The energy humps for these cases have not yet been measured; but they will be determined as soon as possible. Phenylhydroxylamine and nitroso benzene is a completely reversible system and likewise hydroquinone and quinone.[10]

If enzymes or bacteria convert an irreversible oxidation-reduction system into a reversible one, the system will then give an electromotive force with a platinum electrode. This was realized by Cannan, Cohen and Clark [11] more than ten years ago. The only thing that they lacked was the concept of the energy hump.

"[Cell] suspensions act as if there were present very small quantities of active poising material fed from a large reserve which is mobilized slowly but decidedly. Thus a reasonable interpretation of the potentiometric observations we have reported with cell catalysts would seem to be that the catalyst affects the mobilization. The full import of such an effect cannot be appreciated until the electrochemical formulation

[9] Bancroft and Magoffin, *J. Am. Chem. Soc.*, **58**, 2187 (1936).

[10] Glasstone and Hickling, "Electrolytic Oxidation and Reduction," 159 (1936).

[11] Cannan, Cohen and Clark, U. S. Public Health Reports, Suppl. **55** (1926).

of oxidation-reduction can be extended to the so-called irreversible systems which comprise the greater part of organic chemistry," p. 24.

"It would seem that there exist catalysts whose function is an activation of a sort that would result in making a substance electromotively active. Indeed, this is partially implied in certain theories of the function of polar catalysts. Perhaps our experiments indicate that it would be worth while to search for evidence of this sort of activation," p. 25.

"Upon platinized electrodes the potential of a hydrogen electrode is induced in sugar media by cultures such as *Bact. coli* which may liberate hydrogen under proper conditions. Perhaps this might be expected as a natural and insignificant consequence of the juxtaposition of hydrogen and platinum black. But, in the present state of our knowledge, it is equally legitimate to suggest that the appearance of hydrogen harmonizes with the attainment of that reduction intensity at which hydrogen should be liberated. Indeed, it seems to require this more comprehensive point of view to maintain perspective when, on the one hand, certain cultures induce a definite over-voltage with the hydrogen which is liberated at considerably less than one atmosphere pressure and when, on the other hand, certain other cultures induce various potentials more positive than that of the hydrogen electrode but no less distinctive," p. 27.

Borsook and Schott [12] have improved on the earlier work of Thunberg [13] and of Lehmann [14] and have shown that the succinic-fumaric system gives a measurable electromotive force in presence of a suitable enzyme. We had not read these papers when we made the prediction [15] that such a phenomenon must occur.

Barron and Hastings [16] showed that electromotive forces can also be obtained for the lactate-pyruvate system, though they did not actually wait for equilibrium to be reached, preferring to add dyes to the system. They say: "There

[12] Borsook and Schott, *J. Biol. Chem*, **92**, 535 (1931).
[13] Thunberg, *Skand. Arch. Physiol.*, **46**, 339 (1925).
[14] Lehmann, *Skand. Arch. Physiol.*, **58**, 173 (1929).
[15] Bancroft and Magoffin, *J. Am. Chem. Soc.*, **58** (1936).
[16] Barron and Hastings, *J. Biol. Chem.*, **107**, 567 (1934).

exist in the cell two kinds of reversible oxidation-reduction systems. The first group is made up of electromotively active oxidation-reduction systems, which will play the rôle of oxidizing catalysts if reduced by the oxidizable metabolites of the cell and then reoxidized by atmospheric oxygen. . . . The second group is made up of a number of irreversible oxidation-reduction systems which become reversible when activated by the activating coenzymes (Wieland's dehydrogenases). These reversible systems are quite different from the first group. They are sluggish reversible systems, which do not readily transfer electrons to the electrode and whose equilibrium potentials are determined only by the aid of electromotively active mediators. These systems undoubtedly play an important rôle in those studies in which the reducing intensity of cells has been determined by the aid of reversible dyes," p. 575.

The Helmholtz formula for the relation between electromotive force, heat effect and temperature coefficient was deduced for reversible cells and has hitherto been applied only to them. There seems to be no reason why this limitation should not be dropped, provided we do not do it blindly. Since an electromotive force measures a drop from one energy level to another, it is immaterial whether the operation is reversible or not. We may therefore consider the heat of reaction of an irreversible cell as consisting of a theoretically reversible part and a practically irreversible part, the latter of which may be infinitely small at times, though it probably rarely is. If we calculate a heat effect from the electromotive force and the temperature coefficient, we shall determine the heat effect of the theoretically reversible reaction. The difference between that and the observed heat effect gives the heat effect of the practically irreversible reaction.

If the reaction sulphite to sulphate is theoretically reversible and if the whole irreversibility is in the sulphate to sulphite reaction, the Helmholtz equation will apply without change. It is possible, however, that the change from sulphite to sulphate may consist of a reversible electrolytic portion and a non-electrolytic portion, which would therefore be irreversible electrolytically. This possibility was suggested by Conant

and Lutz.[17] In this case the Helmholtz formula will not apply to the whole reaction and we shall have to determine what the electrolytically reversible and the electrolytically irreversible reactions are. Experiments along this line will be started in the Cornell Laboratory as soon as possible. Such a treatment of the Helmholtz equation is legitimate in a formal way. Whether it will be helpful is yet to be determined.

NITRATES.

Erich Müller[18] has studied the electrolytic reduction of weakly alkaline potassium nitrate solutions at different cathodes. With a normal potassium nitrate solution and a cathode current density of 0.1 amp./cm.^{2} at 15°–20°, and following the reaction gas analytically, he obtained percentage reductions of 14.8, 76.5, 97.6 and 96.8 at cathodes of platinized platinum, smooth platinum, iron, and zinc respectively. The low percentage reduction at a platinized platinum cathode must be a case of the misleading experiment,[19] because Gladstone and Tribe[20] had shown, twenty-three years earlier, that platinum black and molecular hydrogen reduce a potassium nitrate solution to ammonia and caustic potash. Consequently, one must get 100 per cent. current efficiency and not 15 per cent. if one electrolyzes a normal potassium nitrate solution at a platinized platinum cathode with a sufficiently low current density. Müller's own experiments are not consistent. He determined decomposition voltage curves for normal potassium nitrate plus twentieth-normal caustic potash and found that the value at a platinized platinum cathode is a little less than at a smooth platinum cathode, and that both values are a little less than the hydrogen value.

It seemed probable that Müller's abnormal value of 14.8 per cent. current efficiency was due to an adsorption of ammonia by the platinum black, poisoning the cathode to a considerable extent. We, therefore, determined decom-

[17] Conant and Lutz, *J. Am. Chem. Soc.*, **45**, 1047 (1923); Conant, *Chem. Reviews*, **3**, 4 (1926).

[18] E. Müller, *Z. anorg. Chem.*, **26**, 1 (1901).

[19] Bancroft, *The Rice Institute Pamphlet*, **15**, 224 (1928).

[20] Gladstone and Tribe, *J. Chem. Soc.*, **33**, 309 (1878).

position-voltage curves for different cathodes with neutral solutions of sodium nitrate saturated at room temperature. In all runs the anode was a smooth platinum foil, 1.7 × 2.5 cm. The platinized platinum foil cathode was also 1.7 × 2.5 cm. The zinc, amalgamated zinc, and iron strip cathodes were 1.3 × 2.5 cm., while the mercury cathode had a diameter of 0.6 cm. In all runs the electrodes were 3.5 cm. apart.

The break-point for a saturated sodium sulphate solution was 2.15 volts and 0.002 amp. with a platinized cathode, 2.80 volts and 0.003 amp. with a zinc cathode, both at 25°. In Table I are given condensed data for neutral and slightly

TABLE I.

Break-points for Saturated Sodium Nitrate.

The first figures indicate the point at which oxygen begins to come off; the second figures indicate the point at which hydrogen begins to come off.

Platinized Platinum 25°		Platinized Platinum 80°		Iron 25°	
Volts	Amps.	Volts	Amps.	Volts	Amps.
2.15	0.002	1.34	0.001	2.12	0.004
2.70	0.018	2.60	0.057	4.20	0.680

Zinc 25°		Amalgamated Zinc 25°		Mercury 25°	
Volts	Amps.	Volts	Amps.	Volts	Amps.
2.40	0.005	2.80	0.004	2.90	0.002
4.40	0.640	3.60	0.180	5.20	0.230

Break-points for Saturated Sodium Nitrate, N/100 with Respect to NaOH.

Platinized Platinum 25°		Zinc 25°	
Volts	Amps.	Volts	Amps.
1.28	0.001	2.18	0.002
2.45	0.005	4.25	0.530

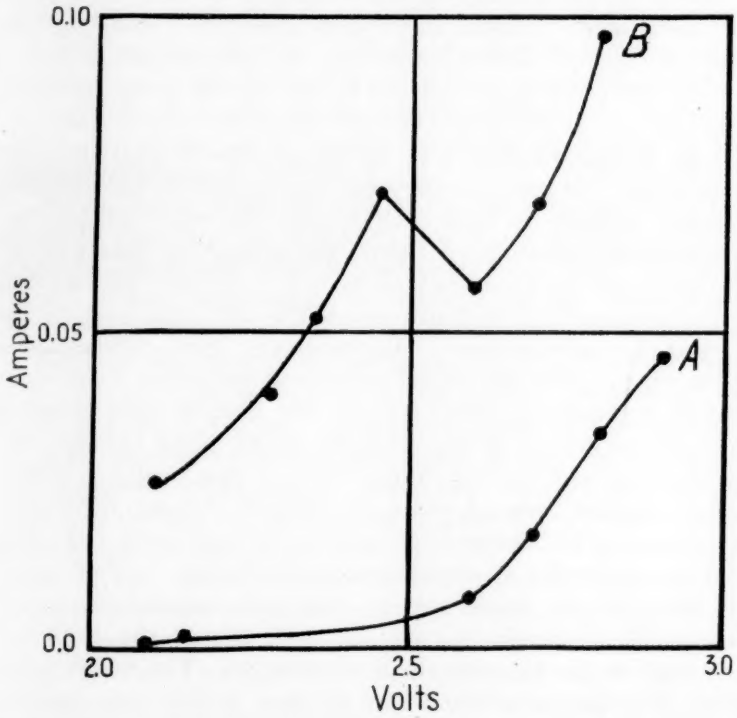
alkaline solutions of sodium nitrate with cathodes of platinized platinum, smooth platinum, iron, zinc, amalgamated zinc, and mercury.

Examination of the decomposition-voltage curves, Fig. 1, for the neutral sodium nitrate solution with platinized-platinum cathodes shows that we have a system behaving like the sodium chlorate one.[21] At 25° there is no downward break in the curve; but one is quite clear at 80°. The first part of the curve at 80° represents the reduction of nitrate,

[21] Bancroft and Magoffin, *J. Am. Chem. Soc.*, **57**, 2563 (1935).

while evolution of hydrogen takes place as well over the latter part. The apparent passivity is caused by the impoverishment of sodium nitrate in the pores of the platinized cathode. Müller should have been on his guard in regard to this, because Gladstone and Tribe had shown that platinum black adsorbs ammonia.

FIG. 1.



Current-voltage curve for sodium nitrate. $A = 25°$, $B = 80°$.

Though the showy thing is the break in the 80° curve, the really important one is the very small difference in the current necessary to set free hydrogen in the 25° curve, two to eighteen milliamperes. The current density would have to be held very low in order to keep the current efficiency high and that is what Müller found without knowing it. In the

slightly alkaline sodium nitrate solution a current of only five milliamperes sets free hydrogen.

Another interesting thing, which also appears from Müller's data, is that the voltage at which the reduction starts varies with the nature of the cathode. It is 2.15 volts for platinized platinum, 2.12 volts for iron, 2.40 volts for zinc, 2.80 volts with amalgamated zinc, and 2.90 volts with mercury. Amalgamating the zinc makes it behave more like mercury, changing it a good deal although this has no effect on the electromotive force of a zinc electrode. Making the solution slightly alkaline lowers the voltage somewhat.

The difference in voltage due to varying the cathode means a variation in activation of the nitrate or an existence of overvoltage in the solution, just as one prefers to word it. Although the voltage necessary to reduce sodium nitrate at a mercury cathode is higher than that necessary to set free hydrogen at a platinum cathode, the voltage necessary to set free hydrogen at a mercury cathode is relatively greater still and consequently a mercury cathode is more efficient than a platinized platinum one. Although the iron cathode does not seem to lower the initial voltage of reduction much over that of a platinized platinum one, the current that passes is so much greater at an iron cathode at any given voltage that the iron cathode is the most efficient practically. Müller found another form of the same thing. Taking three cells in series so as to get the same current through each, and using smooth platinum, zinc and iron as cathodes, Müller found 42, 181 and 187 milligrams of ammonia respectively in the three cells, although the voltage drop across the terminals was least in the cell with the iron cathode. The depolarizing effect of a nitrate solution was greatest at the iron cathode.

Müller has made a series of determinations of cathode potentials during electrolysis at different cathodes in solutions normal with respect to sodium nitrate or sodium nitrite and hundredth-normal with respect to sodium hydroxide. He gives no directly observed figures, only what he calls absolute cathode potentials. This should mean the Ostwald zero; but he takes the tenth-normal calomel electrode as -0.59 volts, which is not what Richards made it. We shall follow the

example of Foerster [22] and of Kremann and Müller,[23] adding 0.26 volts to Müller's figures and reversing the sign. This gives data which are, as near as may be, in terms of the hydrogen electrode as zero. As there are apparently very marked differences in the evolution of hydrogen from potassium sulphate solutions at iron cathodes, the data may be considerably in error.

Müller found approximately − 0.65, − 0.70, − 0.86 and − 1.10 volts respectively for the initial reduction of weakly alkaline nitrate to nitrite at cathodes of platinum, iron, zinc, and mercury respectively. Since the corresponding values for hydrogen are approximately − 0.68, − 0.90, − 1.01 and − 1.30 volts, it is evident that nitrate will be reduced to some extent to nitrite at all these cathodes, and this is true experimentally.

If we know what electromotive force a nitrate-nitrite electrode should give, supposing one could be made to function, we should be able to calculate the energy hump for nitrate with some degree of approximation. Pick [24] has calculated a value of + 0.01 volt for a nitrate-nitrite electrode in alkaline solution. This value is not strictly comparable with that of − 0.65 volt found by Müller because the alkalinity is not the same. Subject to an unknown correction for this, the energy hump for nitrate in alkaline solution is the algebraical difference of these two values, or about 0.7 volt at platinum. If the platinum cathode activates nitrate to any extent—as it undoubtedly does—the true energy hump in the absence of the electrode is still larger. It is apparently about 0.9 volt at a zinc cathode and about 1.1 volts at a mercury cathode. This shows an activation of sodium nitrate by platinum over mercury of about 0.4 volt.

Another striking case of adsorption and activation was studied fifteen years ago by Conant and Cutter [25] who did not, however, recognize it as such. Dimethylacrylic acid is reduced readily by hydrogen at a platinum cathode in an acid

[22] Foerster, "Elektrochemie wässeriger Lösungen," 585 (1922).

[23] Kremann and Müller, Ostwald's Handbuch der allgemeinen Chemie, **8** II, 333 (1931).

[24] Pick, *Z. Elektrochemie*, **26**, 186 (1920).

[25] Conant and Cutter, *J. Am. Chem. Soc.*, **44**, 2651 (1922).

solution. It is not reduced by a chromous chloride solution, even though this is a stronger reducing agent than platinum and hydrogen by about 0.3 volt. Evidently the platinum activates the dimethylacrylic acid.[26] This could be tested easily but has not yet been done. If platinum is held in a suitable chromous chloride or acetate solution until all the hydrogen is given off that will come off in a reasonable time, we predict that the solution will reduce dimethylacrylic acid in the presence of platinum. It is not yet necessary to differentiate in principle between hydrogenation and reduction.

CHLORATES.

Chloric acid is a fairly powerful oxidizing agent, at least as strong as chromic acid; but neutral chlorates have little or no oxidizing power at ordinary temperatures—much less than hypochlorite solutions in spite of the higher oxygen content. We explain the relative inertness of the neutral and alkaline solutions by postulating an energy hump. Since this explanation can be used to account for anything, we must show independently the existence and magnitude of the hump. Fortunately this can be done very satisfactorily in the case of the chlorates.

In a previous paper[27] it was shown that pulverulent copper activates neutral chlorate so much that hydrazine[28] reduces it quantitatively to chloride, whereas even boiling hydrazine does not reduce chlorates in the absence of copper. Hofmann[29] showed that osmium tetroxide activates sodium chlorate so much that one gets a potential difference of + 0.34 volt for a platinum-foil electrode in a solution containing 1 g. $NaHCO_3$, 0.5 g. NaCl, 5.0 g. $NaClO_3$ and 0.02 g. OsO_4 per 100 cc. when measured against a tenth-normal calomel electrode. This would correspond to about + 0.39 volt against a normal calomel electrode and means that we have approximately E_h = + 0.69 volt. Not realizing that this was an irreversible reaction Hofmann had no difficulty in measuring this electromotive force. Chlorate can be reduced

[26] Bancroft and Magoffin, *J. Am. Chem. Soc.*, **57**, 2563 (1935).
[27] Bancroft and Magoffin, *J. Am. Chem. Soc.*, **57**, 2563 (1935).
[28] Hodgkinson, *J. Soc. Chem. Ind.*, **33**, 815 (1914).
[29] Hofmann, Ber. **46**, 1662 (1913).

electrolytically at a platinum cathode; but we know that the platinum activates the chlorate. Consequently we are undoubtedly justified in saying that the true value for neutral chlorate in the absence of a metal corresponds to $E_h > -0.36$ volt. Since alkaline sodium hydrosulphite reduces chlorate, the activation by platinum is not much.

The decomposition voltage for chlorate at an iron cathode is apparently about $E_h = 0.46$ volt. Consequently the energy hump for chlorate is at least 1.05 volts (0.36 + 0.69), a trifle less at platinum, and about 0.8 volts (0.36 + 0.46) at iron.

Osmium tetroxide vapor has only a very slight effect on the temperature at which potassium chlorate breaks down when heated and Hofmann believes that the activation is due to compound formation between chlorate and osmium tetroxide. The combination sets free iodine from potassium iodide as it should, but not bromine from potassium bromide. The so-called mercurous oxide—really mercuric oxide and mercury—is converted into mercuric oxide. Soot is oxidized readily to carbon dioxide, mellitic acid and other substances. Ethylene is converted into ethylene glycol; but hydrogen is apparently not attacked. Allyl alcohol is oxidized at 50° to glycerol. Fumaric acid is oxidized to racemic acid and maleic acid to mesotartaric acid; sodium formate to oxalate and carbonate.

While activated chlorate is called by Hofmann a pretty strong oxidizing agent, nobody calls potassium ferricyanide that, and yet molar potassium ferricyanide with platinum gives $E_h = +0.71$ volt. The reason that it does not appear to be so strong an oxidizing agent as activated chlorate is that ferricyanide is a reversible oxidizing agent and chlorate an irreversible one. If one converted ferricyanide into an irreversible oxidizing agent by removing the ferrocyanide as fast as formed, ferricyanide should do all the stunts that activated chlorate will do. Ferric chloride seemed to be the ideal thing for this purpose.

Potassium ferricyanide in molar solution gave a value of $E_c = +0.407$ volt. Addition of 0.1 cc. of a molar solution of ferric chloride to 30 cc. of the potassium ferricyanide solution caused a change to $E_h = +0.881$ volt. We therefore

predicted that a solution of potassium ferricyanide alone would not oxidize sodium formate appreciably; but would do so in presence of ferric chloride.

Twenty-five cubic centimeters of a molar solution of potassium ferricyanide were mixed with an equal volume of molar ferric chloride and one gram of sodium formate added. The control had no ferric chloride. These mixtures were allowed to stand for twenty-four hours. The solution containing the ferric chloride became deep blue, and pasty, while no change in the control tube could be noticed. Both mixtures were filtered and calcium chloride added to the filtrates to determine whether oxalate or carbonate were present. Both tests were negative, which was something of a shock. The blue residue from the solution containing ferric chloride was washed with ammonium hydroxide to remove any carbonate or oxalate which might have been adsorbed. The washings were made acid with acetic acid and tested with calcium chloride. A precipitate of calcium oxalate was obtained.

The experiments were repeated, keeping the solutions in the dark and again a test for oxalate was obtained in the solution to which ferric chloride had been added. Ferric chloride and sodium formate without the ferricyanide gave no test for oxalate or carbonate.

Tommasi [30] reports that potassium perchlorate can be reduced quantitatively to chloride by sodium hydrosulphite, $Na_2S_2O_4$. We have not been able to confirm this statement. Solutions of sodium chlorate and of perchlorate were treated in the cold with sodium hydrosulphite. The excess hydrosulphite was then destroyed with sodium peroxide, the solution made acid with an excess of nitric acid and then tested with silver nitrate. No test for chloride was obtained in either case. The same runs were then made at boiling temperature. This time a test for chloride was obtained in the chlorate solution but not in the perchlorate.

Since the solutions of the sodium hydrosulphite were slightly acid, runs were made in which alkali was added. It was found that sodium chlorate was reduced at room temperature if the solution was neutral or slightly alkaline, and that

[30] Bull. (2) **38**, 148 (1882).

perchlorate was reduced somewhat at boiling temperature if the solution was slightly alkaline. If the perchlorate solution was alkaline enough, quantitative reduction was obtained at boiling temperature.

A dilute solution of potassium perchlorate made alkaline with sodium hydroxide was electrolyzed at 99° with a plain-platinum anode and a zinc cathode. A good test for chloride was obtained, although the reduction was not quantitative. These experiments show that sodium hydrosulphite is a strong enough reducing agent to reduce both chlorate and perchlorate if the pH and the temperature of the solution are adjusted correctly. The reduction is quantitative in both cases if the conditions are controlled properly. Also, boiling solutions of perchlorate can be reduced electrolytically in alkaline solution.

When potassium chlorate is heated by itself in the air, nothing appears to happen until the temperature gets above the melting-point of the chlorate. Oxygen is then set free and some potassium perchlorate is formed. People have adopted [31] the view that two reactions take place independently and simultaneously:

$$(1)\ 2\ KClO_3 \rightarrow 2\ KCl + 3\ O_2,$$
$$(2)\ 4\ KClO_3 \rightarrow \quad KCl + 3\ KClO_4.$$

Equation 1 can be made to take place, one hundred per cent., by adding manganese dioxide. Nobody has yet been able to catalyze Equation 2 or to poison Equation 1 sufficiently to give a one hundred per cent. yield of Equation 2.

In Equation 2 we postulate that all three oxygens are effective in oxidizing potassium chlorate to perchlorate. Fowler and Grant [32] heated potassium chlorate with silver oxide, obtaining potassium perchlorate and metallic silver with practically no evolution of oxygen.

Since no perchlorate [33] is formed when potassium chlorate is heated in contact with manganese dioxide, it seemed to us that this was the way to start studying the phenomenon of the instability of potassium chlorate. When one solid catalyzes

[31] Scobai, *Z. physik. Chem.*, **44**, 319 (1903).
[32] Fowler and Grant, *J. Chem. Soc.*, **57**, 279 (1890).
[33] Eccles, *J. Chem. Soc.*, **29**, 857 (1876).

the decomposition of another solid, the reaction must take place at the solid-solid interface provided we exclude, by definition, the possibility of any appreciable vapor-phase catalysis. Consequently manganese dioxide can only decompose those particles of solid potassium chlorate with which it is in actual physical contact. Since this hypothesis seems not to be covered adequately in the literature, we have made a few preliminary experiments.

The apparatus consisted of a hard-glass test-tube closed air-tight with a stopper which connected by a capillary tube with a Hempel gas-burette. The glass test-tube was immersed in a Wood's-metal bath and the uncorrected temperature was read on a thermometer placed in the bath immediately next to the test-tube. Before oxygen starts to come off, the contents of the test-tube are somewhat cooler than the bath. When oxygen is coming off, the heat of decomposition may easily make the contents of the test-tube somewhat hotter than the bath. Such an error is of no importance so far as general principles are concerned. After each run the test-tube was allowed to cool and all measurements of gas volumes were made at room conditions of pressure and temperature. It was consequently not necessary to know the volume of the test-tube, the exact temperature to which it had been heated, or the temperature gradient.

Anhydrous potassium chlorate, potassium perchlorate and manganese dioxide were ground separately in a mortar to approximately the same particle size. Equal mixtures of potassium chlorate and manganese dioxide or of potassium perchlorate and manganese dioxide were used in all runs. The heating was continued at approximately constant temperature until practically no more gas was evolved.

With potassium chlorate and manganese dioxide at about 225° no more oxygen was evolved after forty-five minutes heating. Ten per cent. of the theoretical amount of oxygen was evolved. At 300° heating was continued for three and one-third hours before evolution of gas ceased. At 330° 96.5 per cent. decomposition was accomplished in twenty minutes and at 335° 98.1 per cent. of the oxygen was evolved in about one minute. Sodeau [34] reports that in his experi-

[34] Sodeau, *J. Chem. Soc.*, **81**, 1074 (1902).

ments "the decomposition became rapid and beyond control when the temperature of the bath had risen to about 340°." In our runs made at 330° and 335° the residue in the test-tube sintered together as though there had been partial fusion. Nothing of this sort was observed at lower temperatures. To check this, a rough determination was made of the eutectic temperature for potassium chloride and chlorate (no manganese dioxide) with the thermometer bulb in the salt mixture. The value was approximately 338°. A mixture of potassium perchlorate and manganese dioxide was heated at 340° for a period of forty-five minutes with only a very slight evolution of gas. The apparent decomposition was about three per cent., which may have been due to traces of potassium chlorate in the perchlorate.

From the experiments it is clear that only that chlorate is decomposed which comes in contact with manganese dioxide. At any temperature below the actual fusion point of the mixture only the surface of the chlorate crystals is decomposed. The remainder of the chlorate crystals is kept from contact with the manganese dioxide by the film of potassium chloride that is formed on the surface of the potassium chlorate crystals. When the temperature is reached at which the mixture melts, the manganese dioxide can then come in contact with all of the potassium chlorate and thus complete decomposition occurs. This temperature is about 335° ± 5°, whereas the initial temperature of decomposition is about 210°. Balarew [35] found the eutectic at about 340°.

Balarew found no trace of chloride formation after the mixture had stood for a year at room temperature; but new chloride could be detected after an hour's heating at 140°. Balarew believes, however, that "only softened or molten potassium chlorate decomposes catalytically with measurable velocity."

Balarew [36] claims to have found that the presence of an unspecified amount of water vapor lowers the temperature at which oxygen begins coming off by about 12°. It does not seem probable that the mixture of potassium chlorate

[35] Balarew, *Z. anorg. allgem. Chem.*, **143**, 89 (1925).
[36] Balarew, *Z. anorg. allgem. Chem.*, **145**, 121 (1925).

and manganese dioxide can take up much water at high temperatures. It is more likely, therefore, that the effect, if real, is due to a change in dispersion of the potassium chlorate or of the manganese dioxide by water adsorbed at the lower temperatures.

The catalytic decomposition of potassium chlorate is similar in principle to the decomposition of alcohol at the surface of heated nickel or alumina, except that the alcohol is a vapor under the conditions of the experiment, whereas the potassium chlorate is a solid or a liquid, depending on the temperature. It is precisely similar to the case of silver oxide, the decomposition of which is accelerated by contact with metallic silver. There is no justification at present for postulating higher oxides or intermediate compounds, real or otherwise. It is a plain case of adsorption with activation. Marc [37] showed that solid silver selenide catalyzes the conversion of Selenium B into Selenium A. He considered that this was the first case of heterogeneous catalysis in solid systems. Marc had forgotten that one can get oxygen from potassium chlorate in presence of manganese dioxide without fusing any portion of the mass.

We know that hydrogen is activated when adsorbed by platinum or nickel, and that silver oxide is activated when adsorbed by silver; we know that FeO_3 is stabilized when adsorbed by iron. We cannot predict whether we shall get activation or stabilization by adsorption. Contact catalysis is mysterious; but we wish to stress the fact that the catalytic action of manganese dioxide on potassium chlorate does not differ in principle from hundreds of other cases of contact catalysis. It is the general case that is mysterious and not the special cases. The catalytic decomposition of potassium chlorate is no more mysterious—and no less mysterious—than the hydrogen electrode; but it is very difficult to convince people of that.

Since the oxygen is given off at the manganese dioxide interface, there can be no potassium perchlorate formed and actually none is formed. Since manganese dioxide does not decompose perchlorate appreciably at 340°, the catalytic

[37] Marc, *Z. anorg. Chem.*, **85**, 65; Berger, 75 (1914).

decomposition of potassium chlorate by manganese dioxide below 340° does not involve the formation of potassium perchlorate as a transitory stage.

OVER-VOLTAGES.

In 1916 Bancroft [38] wrote: "Peters [39] showed that platinum accelerated the evolution of hydrogen from a chromous chloride solution and Jablczynski [40] showed that mercury had no such action. It was considered that platinum catalyzed the reaction and that mercury did not. To-day we say that hydrogen is set free at the platinum because of the low over-voltage and is not set free at the mercury because of the high over-voltage. The advantage of the latter point of view is that it shows the desirability of trying other metals with chromous chloride solution so as to find out at what degree of over-voltage the hydrogen ceases to be evolved rapidly."

The next year Forbes and Richter [41] published a paper on the chromic-chromous potential at mercury electrodes. They point out the importance of using pure mercury. "Lewis [42] has shown the vital necessity of the highest degree of purity in mercury if evolution of hydrogen is to be avoided at potentials comparable with those measured by us. Peters and Mazzuchelli [43] both noted such an evolution on mercury in contrast to our own experience when using pure mercury. McBain [44] also states that pure mercury does not decompose solutions of chromous chloride."

Forbes and Richter found that "referred to normal hydrogen electrode as zero, with correction for junction potentials,

$$\pi = -0.400 + 0.065 \log Cr^{III}/Cr^{II}.$$

On platinum, potentials reached a maximum about 0.16 volt lower, with evolution of hydrogen." This difference cannot be due to the same cause as the difference studied by Mi-

[38] Bancroft, *J. Phys. Chem.*, **20**, 399 (1916).
[39] Peters, *Z. physik. Chem.*, **26**, 217 (1898).
[40] Jablczynski, *Z. physik. Chem.*, **26**, 117 (1898).
[41] Forbes and Richter, *J. Am. Chem. Soc.*, **39**, 1140 (1917).
[42] Lewis, *Proc. Am. Acad.*, **41**, 399 (1906).
[43] Mazzuchelli, *Gazz.*, **31**, II, 374 (1901); **35**, I, 417 (1905).
[44] McBain, Inaugural Dissertation, Heidelberg (1909).

chaelis [45] with the cysteine electrode. Forbes and Richter apparently observed all due precautions in regard to the absence of oxygen.

In order to determine the maximum reducing power of chromous chloride we have made electromotive force measurements similar to those of Forbes and Richter but not with the very specially purified mercury that they used. It is only necessary that the over-voltage at the mercury be larger than the potential difference due to the chromous salt. Because of the ease with which chromous chloride is oxidized, these determinations had to be made in the absence of air. The apparatus consisted of a 250 cc. cylinder fitted with a rubber stopper, the connection being made air-tight. The stopper had three holes bored in it: one for the salt bridge leading to the calomel electrode; one for the second electrode; and one for an escape tube for any gases that might be formed in the cell. The other end of the escape tube was kept beneath water to keep any air from diffusing back into the cell. The cell was charged with chromic chloride, hydrochloric acid and zinc. The zinc reduced the chromic chloride as far as might be to chromous chloride, the electromotive force of which was then measured. In all runs the hydrochloric acid concentration was molar. Measurements were made with 1 M and 0.1 M chromous chloride with platinum and mercury electrodes, and with M/10 chromous chloride at a copper electrode. The data are given in Table II. The electromotive forces have been converted from the calomel to the normal hydrogen as zero by subtracting 0.3 volt.

TABLE II.

Electromotive Forces of Chromous Chloride Cells.

The calomel electrode is always cathode.

Cell.	E_c.	E_h.
Hg|M $CrCl_2$ + M HCl|Calomel	−0.728	−0.428
Hg|M/10 $CrCl_2$ + M HCl|Calomel	−0.663	−0.363
Cu|M/10 $CrCl_2$ + M HCl|Calomel At beginning of run	−0.634	−0.334
After 5 days (no more H_2 being evolved)	−0.569	−0.269
Pt|M/10 $CrCl_2$ + M HCl|Calomel At beginning of run	−0.456	−0.156
After 3 days (no more H_2 being evolved)	−0.363	−0.063
Pt|M $CrCl_2$ + M HCl|Calomel	−0.694	−0.394

[45] Michaelis and Flexner, *J. Biol. Chem.*, **79**, 689 (1928).

The measurements indicate that chromous chloride is a stronger reducing agent than hydrogen by 0.36 and 0.42 volt in 0.1 M and M solutions. With platinum and copper electrodes such a difference cannot be realized because both platinum and copper catalyze the reaction between hydrochloric acid and chromous chloride.

The fact that the electromotive force measured at a mercury electrode remains constant for a long time, while that measured at platinum or copper falls off gradually, indicates that the mercury does not catalyze the reaction between hydrochloric acid and chromous chloride to amount to anything, whereas platinum and copper do catalyze the reaction appreciably. Furthermore, since the evolution of hydrogen ceases at the copper electrode and at the platinum electrode when the electromotive forces have dropped approximately to those of the hydrogen over-voltages at copper and platinum respectively, we draw the important conclusion that the catalytic action of metals on the reaction between chromous chloride and acids or water depends on the hydrogen over-voltage of the metal in question. If the hydrogen over-voltage of the metal being used is lower than the electromotive force of the chromous salt solution in which it is immersed, hydrogen will be liberated at the surface of the metal. The liberation of hydrogen will continue practically until the electromotive force of the chromous chloride is just equal to the hydrogen over-voltage of the metal, at which point it will cease in the ordinary sense of the term. If the hydrogen over-voltage of the metal being used is greater than the electromotive force of the chromous chloride solution in which it is immersed, practically no hydrogen will be liberated and the electromotive force of the solution will remain constant, provided no air is admitted.

Practically, things will happen as described; but, theoretically, the matter is probably somewhat different. We say ordinarily that no hydrogen is set free at a mercury cathode at a voltage below that of the over-voltage of hydrogen defined. If, however, one were to polarize a mercury electrode for a long time to less than the value at which we ordinarily speak of hydrogen being evolved, it is probable that some hydrogen would actually be evolved. If we consider the

surface as polarized with monatomic hydrogen, that monatomic hydrogen will undoubtedly polymerize at some rate. Since hydrogen at a mercury electrode does not give an electromotive force corresponding to the over-voltage, there can be no reverse reaction under these conditions.

We do not know whether this reasoning would or would not apply to the theory of over-voltage developed by Gurney,[46] using the concepts of quantum mechanics.[47] "It is supposed that for an ion to be discharged at a cathode, electrons must pass over, or through, an energy barrier from the metal into a vacant quantum level of *equal* energy in the ion to be discharged. If the energy of the vacant level in the ion happens to be higher than the highest occupied level in the atom, then the transfer cannot occur and the ion cannot be discharged."

Since the chromous-chromic chloride solution is relatively stable in contact with mercury and by itself, there must be what amounts to an over-voltage for hydrogen even in the absence of an electrode. It seems to us that this value must be higher than that obtained at any metal. If this were not so, the setting-free of hydrogen would be catalyzed by the solution in contact with the electrode. Stone and Beeson [48] state that chromous sulphate solutions are practically stable in the absence of platinum. This brings up a question which has never been studied experimentally. To what extent is the over-voltage at any metal a function of the other ions and constituents of the solution?

We know that some titanous solutions [49] will break down in contact with platinum, setting free hydrogen. Experiments were therefore made with titanous chloride solutions, using the same apparatus as in the chromous chloride solutions. The titanous chloride solutions were molar with respect to hydrochloric acid. The results are given in Table III. The E_h values are obtained by subtracting 0.3 volt from the E_c values.

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[46] Gurney, *Proc. Roy. Soc.*, **134** A, 137 (1931).

[47] Glasstone and Hickling, "Electrolytic Oxidation and Reduction," 61 (1936).

[48] Stone and Beeson, *Ind. Eng. Chem. Anal. Ed.*, **8**, 188 (1936).

[49] Diethelm and Foerster, *Z. physik. Chem.*, **62**, 129 (1908); Denham, **72**, 641 (1910).

TABLE III.

Electromotive Forces of Chromous Chloride Cells.

The calomel electrode is always cathode.

Cell.	E_c.	E_h.
Hg|M/10 $TiCl_3$ + M HCl|Calomel	−0.384	−0.084
Pt|M/10 $TiCl_3$ + M HCl|Calomel	−0.381	−0.081

It is apparent from the values in Table II that the highest electromotive force obtained with this titanous chloride solution is barely above the hydrogen value at platinum and consequently there will be very little change with the time. The difference of three millivolts in favor of the mercury electrode is probably real. Diethelm and Foerster obtained a value of $E_h = -0.023$ volt for N/2 titanous oxide in 4 N sulphuric acid, a result which agrees satisfactorily with ours when one remembers the lower concentration of titanium salt, the higher concentration of sulphuric acid, and the 98 per cent. reduction of TiO_2. Time did not permit of a study of copper electrodes. This must be made some time, because the decomposition-voltage curves for copper cathodes, as found by Diethelm and Foerster are a bit puzzling.

Similar experiments were made with sodium hydrosulphite, $Na_2S_2O_4$, in solutions 0.08 M with respect to sodium hydroxide. The data are given in Table IV.

TABLE IV.

Electromotive Forces of Sodium Hydrosulphite Cells.

The calomel electrode is always cathode.

Cell.	E_c.	E_h.
Cu|M/10 $Na_2S_2O_4$ + 0.08M NaOH|Calomel	−0.988	−0.688
Pt|M/10 $Na_2S_2O_4$ + 0.08M NaOH|Calomel	−0.922	−0.622

Since the hydrogen electrode in 0.1 M NaOH has a value of about $E_h = -0.734$ volt, neither solution can set free hydrogen and consequently sodium hydrosulphite in this solution is not as good a reducing agent as hydrogen. We have no data on more concentrated and more alkaline solutions. We also offer no explanation at present for the different voltage with a copper electrode.

SUMMARY.

1. When a reaction is permitted by the free energy relations but cannot take place unless and until some molecules

of the reactants are raised to an energy level higher than that attained by any molecules of the reactants under ordinary conditions, we say that the system has to pass an energy hump for the reaction to take place.

2. The concept of the energy hump is a normal extension of the concept of the energy of activation and includes this latter as a special case.

3. When a reaction can be made to take place electrolytically, the height of the energy hump is defined as the difference between the free energy of the system and the voltage energy necessary to produce the reaction. With a glass of water standing on a table the energy hump which keeps the water from running on the floor is given by the distance between the surface of the water and the top of the glass.

4. An energy hump tends to disappear with increasing concentration or rise of temperature as in the case of a sulphuric acid solution. The energy hump may be eliminated by a suitable catalytic agent, as in the case of osmic acid and potassium chlorate or in the case of platinum and molecular hydrogen.

5. A one-way electrode, such as the cysteine-cystine one, gives an electromotive force which, at constant temperature and constant pH, is a function of the concentration of cysteine but independent of the concentration of cystine. The sulphite-sulphate electrode is another of the same type.

6. If an electron transfer between an inert metal and an oxidizable or reducible substance involves an energy hump under the conditions of the experiment, no reduction or oxidation potential will be set up; otherwise one will. A nitrate, sulphate or nitrobenzene electrode gives no oxidation potential. A lead peroxide, permanganate or nitrosobenzene electrode gives one. A cysteine or a sulphite electrode gives a reduction potential, while an alcohol electrode does not.

7. The energy hump for the sulphate-sulphite reaction is at least two volts and may be much more. The energy hump for the nitrate-nitrite reaction in alkaline solution is approximately 0.66 volt at a platinum cathode, 0.7 volt at an iron cathode, 0.9 volt at a zinc cathode, and 1.1 volts at a mercury cathode. It will be higher still in the absence of a cathode. The energy hump in a chlorate solution appears to be at least

1.05 volts at a platinum cathode, at least 0.8 volt at an iron cathode, and zero at a platinum cathode in presence of osmium tetroxide.

8. Potassium chlorate is adsorbed and activated by manganese dioxide just as silver oxide is adsorbed and activated by silver. There is no justification at present for postulating any higher oxides of manganese, real or hypothetical, as taking part in the reaction. Only the potassium chlorate in actual physical contact with the manganese dioxide reacts. When the eutectic temperature is reached, $335° \pm 5°$, the manganese dioxide can come in contact with all the potassium chlorate and the reaction runs to an end.

9. When the electromotive force of a chromous chloride solution is higher than the over-voltage of hydrogen at the immersed metal, the chromous chloride will oxidize until approximate equilibrium is reached. A chromous chloride solution which is 0.4 volt negative to hydrogen will stay practically constant with mercury, will drop somewhat with copper, and will drop more with platinum. The fact that a chromous chloride solution decomposes slowly or not at all in the absence of a metal catalyst proves that there is an over-voltage for hydrogen even in the absence of a metal.

10. The reduction of dimethylacrylic acid by platinum and hydrogen when it is not reduced by a chromous chloride solution is due to the fact that platinum activates the dimethylacrylic acid. It is not a question of a difference between reduction and hydrogenation.

Large Generator Shaft Extracted with Dry Ice.—(*Power Plant Engineering*, Vol. XLI, No. 7.) The value of "dry ice" for dismantling and assembling major shrunk-fits has been definitely established at the Queenstown hydro generating plant of Niagara Falls, Ontario, where a 40-ton steel shaft has been extracted from a 270-ton rotor of a 55,000 kva. hydro-electric generator by cooling the shaft with a mixture of dry ice and alcohol. The freezing mixture was placed in a tank and consisted of 350 gallons of alcohol and 3 tons of carbo-ice. The shaft is 363 inches long, about 32 in. in diameter, and has an 8-inch bore throughout its length. The mixture was circulated by pumping it through the hollow shaft so as to cause the shaft to freeze. The temperature of the mixture reached − 97 deg. F. In about two hours the shaft was completely free of the rotor. After the shaft has been repaired it will be replaced by the same procedure.

R. H. O.

EARLIEST WIRELESS EXPERIMENTS IN AMERICA.

Elihu Thomson Played With Idea Over Half Century Ago.

BY

NATHAN G. GOODMAN.

The death of Elihu Thomson, pioneer in electrical development and dean of the engineering staff of the General Electric Company, on March 13, 1937, has led to some speculation as to the first experiments with wireless telegraphy in this country. Thomson was known largely as the originator of electric arc welding and as the principal organizer of the Thomson-Houston Electric Company in 1883, which was later merged with the Edison General Electric Company, which ultimately became the General Electric Company of today. He held no less than 800 patents. Out of his constructive mind came the repulsion type of induction electric motor, the magnetic blow-out principle in lightning arresters and electric switches, and the oil-cooled type of transformer.

The true story of Thomson's first experiments with wireless is revealed in a letter written in the spring of 1922. "Mr. Edison, in 1875, made some experiments with electromagnets, and found what he called a new force, and named it 'Etheric Force,'" he said. "A Dr. George M. Beard wrote up the matter for the newspapers. It was believed to be a new force because it did not deflect a galvanometer needle, and did not give any evidences of polarity, and seemed to pass through insulators, such as blocks of paraffin." The inventor then discusses the matter in detail:

"I suggested to Professor Edwin J. Houston, who was then teaching physics in the school [the Central High School of Philadelphia], while I was in the chemistry department, that there was no new force concerned, but merely electrical phenomena, and that by a few experiments this could be definitely shown. These experiments were made at the Central High School with the apparatus we had at disposal, and the results were published in the JOURNAL OF THE FRANK-

LIN INSTITUTE. The article was reproduced in the *Scientific American Supplement* of May 20, 1876. It was there definitely shown by the experiments that the so-called 'Etheric Force' was merely a rapidly reversed discharge. We not only succeeded in obtaining it in other ways than those laid down in the Edison experiments, but also obtained the so-called 'Etheric Force' in opposite phases, so that these could be united and neutralize each other; or in other words, that there was electric plus and minus polarization concerned. . . .

"I then suggested to Professor Houston that we should make further experiments and magnify the effects greatly. The school possessed a Ritchie 6″ spark Ruhmkorff coil, and a plunge battery for exciting it. This was made use of in the following way, and it was set up on the lecture table in Prof. Houston's room on the first floor of the old High School at Broad and Green Streets, and one of the terminals of the coil was directly connected to the water supply pipe just under the edge of the table by a wire about two feet long. The other terminal was connected by a wire five or six feet long to a hollow tin vessel mounted a distance away upon a large glass jar on the table, which jar effectively insulated it. The in vessel was really a part of the water still used in the chemical laboratory, of which I had charge. The terminals were set so that on operating the coil, sparks of about 2″ in length jumped between them. Here, it will be seen, one has all the elements of a wireless transmission of the spark variety. Then, explorations were made all over the building, even to the observatory, for the presence of the waves which were sent out at each spark, and the indications were found to be obtainable everywhere from metallic objects throughout the building, and I knew perfectly well that the same would be true if I had gone outside the building down the street hundreds of feet away. There were brick walls and solid floors between the lecture room, where the coil was operated, and the other parts of the building.

"The only detector then available was that which Edison had used in his 'Etheric Force' experiments; namely, two finely pointed black-lead pencil tips, brought together with the lightest possible contact, and shaded from the light. A tiny spark was sent whenever the coil was operated, one point

being, say, attached to a door knob, and the other in contact with the hand that was manipulating it.

"Professor Houston wrote up an account of some of these experiments which appeared in the JOURNAL OF THE FRANKLIN INSTITUTE, April, 1876, under the title, 'Experiments with Ruhmkorff Coil and Spark.' I do not think he fully realized just what we had been doing, or realized it as I did, for he did not in this account emphasize, as was proper, the really novel things which had been done. However, Professor Monroe B. Snyder, then in charge of the [astronomical] observatory, was a witness of the experiments, and quite interested in them, and so far as I know, he is the only living man now,[1] aside from myself, who was concerned with them. Under the title 'Professor Elihu Thomson's Early Experimental Discovery of the Maxwell Electro-Magnetic Waves,' Professor Snyder wrote an article which appeared in the [Central] High School *Mirror* in November, 1919, giving his recollection of the early experiments, and this article by Professor Snyder was reproduced in the *General Electric Review* of 1920, volume 23, page 208. . . .

"Subsequent to this work, my whole time and attention was taken up in developing the Thomson-Houston electric lighting system, its manufacture, etc., and the subsequent developments in other forms in lighting, motor power, railways, electric welding and the like, but on a number of occasions I have referred to the future possibilities in transmission by Hertzian waves, since Hertz in 1887 had published his comprehensive study of them. I recognized the possible applications, and in a lecture here in Lynn in what is known as the Cobbett School, which lecture dealt with electric waves generally, I made the positive prediction that these waves would be used in transmission of intelligence, especially over the sea, and pictured the lighthouse of the future as having an equipment for the purpose. This was in 1889. In an article in the now defunct *New England Magazine*, on the 'Future Electrical Development,' and in the issue of July 2, 1892, I stated: 'It may be remarked here, however, that electricians are not without some hope of signalling or telegraphing without wires, even through dense fog, and this may be an

[1] Died September 27, 1932.

accomplished fact soon. Signalling or telegraphing without wires is no new proposal, and there have been many such proposals which are extravagant and impracticable. The fact is, however, that the essential means are not yet forthcoming.' This was true at the time, because the Branly coherer had not been used, and there was the need of a very sensitive detector, which, in our early experiments way back, was not present. This was some years prior to Marconi's announcement of the first solution of the problem.

"I remember, however, very distinctly a conversation I had with the late Dr. Sylvanus P. Thompson, whose fame in the electrical field is world wide as the author of some of the very best text-books on the subject, in which, in 1893, at the World's Fair at Chicago, I maintained that wireless transmission was perfectly possible, and that it would soon come into existence. He disagreed with me, and thought that the apparatus necessary would be too gigantic. I had, in the meantime, worked out the method of the 'singing arc' for maintaining a continuous wave train where the discharge gap is shunted by inductance and capacity, which can be varied. This afterwards was brought out in a slightly different form by Duddell in London, and called by his name, and later by Poulsen, as the Poulsen arc, and applied to wireless transmission. I had worked out the 'singing arc' about 1892, and it is described in United States Patent 500,630, dated July 4, 1893, and entitled, 'Method and Means for Producing Alternating Currents.' That patent was filed July 18, 1892, after the experiments had been carried on. A typical claim from this patent is as follows: 'The method of producing alternating currents or discharges consisting of using a circuit of high self-induction, rupturing said circuit at the spark gap, and diverting said current through a shunt containing a condenser and a self-inducing coil, substantially as described.'"

This letter deserves a place in the history of wireless telegraphy.

PHOTOELECTRIC PHOTOMETRY IN THE PRINTING OF AMATEUR NEGATIVES.[1]

BY

CLIFTON M. TUTTLE.

The successful use of photoelectric devices in the solution of many problems of light measurement and control invites the inventor and engineer to inquire into the possibilities of automatizing certain phases of photographic work. The problem of picture making, stripped of its artistic attributes, appears amenable to measurement. In the purely objective sense, the sole object of photography is to reproduce in the print the brightness relations of the original object. Both the original and the end result may be photoelectrically photometered. Since the physical and chemical processes which lead from the original to the end result are controllable (each within its limits), the adaptation of photoelectric measurement to the control of the variables within these processes so as to produce an end result photometrically comparable with the original is a tempting field for invention.

In considering from the inventor's point of view the possibilities for automatizing photography, it is logical to start at the end rather than at the beginning of the photographic process. The practical reason is sufficient justification. A photoelectrically controlled printer is easier to design and build than a similar camera because it does not need to be light and portable. It can be more expensive than a camera because of the volume of work which it can accomplish.

The basis upon which photoelectric printing inventions must be founded is a knowledge of the photometric relations between negatives and good prints. One familiar with the characteristics of photographic materials is at once aware that this is not such a simple matter as is the analogous case of the relationships between original objects and negatives which

[1] Communication No. *614* from the Kodak Research Laboratories.

render the object brightnesses in what classical photographic theory considers a perfect manner.

In the photographic sense, a "perfect" paper-printed reproduction of most objects is an impossibility. Correctness of gradation can be secured only in a limited brightness range. The highlight-to-shadow ratio of many objects of amateur photography exceeds the available correct range of the photographic image on paper, and rendering of original tones must therefore be sacrificed for one or both extremes. This is the case even with a correctly exposed negative, while for under- and overexposed negatives other compromises must be made.

In the business of producing amateur pictures, usually called the "photofinishing business," these compromises are made by expert printing machine operators who, in a purely subjective manner, adjust the two variables at their disposal—the printing exposure and the contrast grade of the printing paper. Such experts are, of course, handicapped in their work by a lack of positive knowledge of what the individual customer wants in an individual picture. The best procedure which an expert printer can follow is to adapt his technic to produce as nearly as possible prints which will satisfy the average customer.

The substitution of objective measurements for subjective judgment in the analysis of a negative for the purpose of assigning printing exposure and grade of paper has probably never been attempted on a commercial scale though much has been written on this general subject in the literature of scientific photography. It is to be expected from the nature of the problem that the theoretical discussions are somewhat contradictory. Because of the limitations of the positive material, theories relating negative characteristics with printing exposure and grade of paper must start with an assumption that some definite tonal region—highlight, middle tone, or shadow—of the original object is worthy of the most accurate tone reproduction. Dependent upon the accepted hypothesis, theories may call for negative measurements in any of these regions.

In an experimental investigation such as this, in which the purpose is to find a commercially practical system of applying negative measurements to the amateur printing process, it is

well to abandon, temporarily, the theories of photographic tone reproduction in favor of the empirical results obtainable by conventional methods of statistical analysis. Inductive reasoning on this problem—attempts to generalize from the evidence of specific cases—is of questionable validity. A statistical study of negative characteristics and printing factors should result in an unequivocal answer to the question of whether or not photofinishing based on measurement is commercially practical.

AMATEUR PICTURES.

The first requisite for this job is a true sample of an infinite population of developed amateur negatives. Negatives chosen at random from many sources would not be difficult to obtain but an entirely miscellaneous group is apt to have certain shortcomings which may be avoided by the prospective user of photometric measuring methods. It is legitimate to assume that negative development variation may be avoided to such an extent that all negatives will be of uniform color and degree of development. It is also legitimate to assume that either a single type of negative emulsion is to be used or that if more than one type is used, the development for each type may be individually regulated to obtain always negatives of similar contrast characteristics.

The negatives which have been obtained for this experiment are quite representative of amateur "snapshooting" in other respects. About a hundred amateur photographers in different parts of the country have coöperated by sending their negatives to a central processing laboratory where development control [2] was maintained. The negatives were accumulated over a period of several months so that there is wide variety in subject material, exposure, and other differences attributable to seasonal and geographical variations.

From one thousand negatives, two groups for study were made up by random selection. A group of one hundred forms the basis of most of the subsequent discussion. A second group of five hundred was held in reserve and data therefrom were used to check for possible random sampling variance in the smaller group.

[2] The negative development characteristic is discussed later in connection with the subject of paper contrast selection.

The answers to three questions will decide for the inventor whether automatic printing may be of economic value. These questions are:

What kind of a print does the average amateur want from each negative?

How near does the subjective selection of the professional photofinisher come to filling this want?

How near can objective negative measurements for automatic selection come to filling this want?

The most straightforward and certain answers to the first two questions would be provided if representative groups of both amateurs and professional finishers were allowed to choose what they considered best from all the possible kinds of prints which could be made from all the negatives. Literally, this cannot be done; practically, its equivalent is accomplished by varying both attributes of prints—exposure and contrast—in increments to make up an exhibit composed of a series of steps. In order to allow all possible choices, it might seem that the steps should be so close together as to be imperceptible. As a matter of fact, print quality judgment is not nearly critical enough to require steps as small as the least perceptible one either in printing exposure or in contrast. A series of prints in which each member receives forty per cent. more exposure than its predecessor enables the observer to exercise his discrimination about the best printing exposure in a satisfactory manner. With such a series there is seldom a wish for an intermediate step.

Though it may not be true of all groups of amateur negatives, the number and range of paper grades for these negatives which have all been developed to the same extent may be considerably limited. Three grades of bromide printing paper, commercially known as "normal," "medium," and "contrast," [3] suffice to enable the observer to pick a best contrast print without demanding either an intermediate contrast or one of more extreme softness or hardness.

The technic of preparing the series of sample prints does not need much description except to state that the processes of printing and development were carried out mechanically in

[3] The grade of printing paper can be specified definitely only by its characteristic curve. The curves for the papers used are given later under the discussion of paper contrast selection.

such a way that there was rigid control both in timing of the exposure and in maintaining the constancy of development. Prints were made in a projection enlarger all to the same size to facilitate subsequent handling in the judgment experiment. Each negative was printed at ten different steps. Time of

FIG. 1.

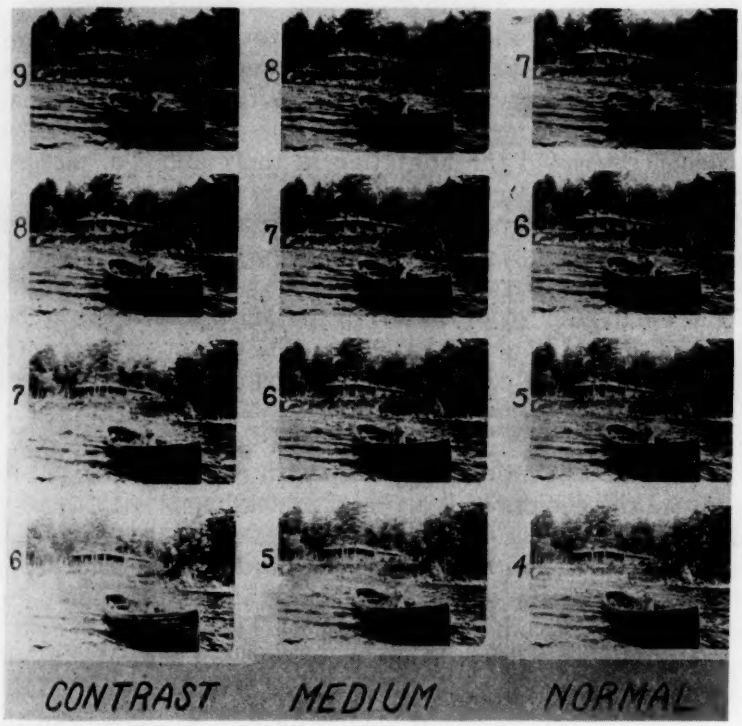


Exhibit of prints of varying quality: decreasing in exposure from top to bottom; decreasing in contrast from left to right.

exposure was kept constant and intensity was varied in increments of 0.15 log intensity units. From the resulting series of prints it was possible to pick in every case a set of four consecutive steps which would carry the picture from definitely too dark to definitely too light.

Sets of twelve prints—four on each grade of paper—were mounted on cardboard in the manner shown in Fig. 1.

PRINT SELECTION.

The smaller group of pictures was submitted to each of eleven typical amateur photographers and to each of six excellent photofinishers. The larger group of 500 was submitted to four of the amateurs and one of the photofinishers. The observers were asked to select: (1) The best printing exposure for each grade of paper. (2) The best print on the best grade of paper.

The process of selection required a total time of about two hours from each observer who could complete only about one quarter of the observations at a single sitting before becoming fatigued. The slowness in getting the data was the factor which necessitated the limitation in the number of pictures and number of observers involved.

One observer repeated his choosing at two different illumination levels (5 foot-candles and 25 foot-candles) with a week's interval between runs. His average choice shifted about a half step (0.07) toward the darker prints at the higher illumination. All observations with this exception were made at an approximately constant illumination of 10 foot-candles.

AMATEUR AND PROFESSIONAL PRINTING EXPOSURE CHOICES.

The first interesting thing to do with these choice data is to compare the choices of individual professionals with those of the amateurs. The average of the eleven amateur exposure selections was computed for each print. The professional printing exposure judgment for each print was then compared with the average amateur judgment. The data are of course too voluminous to show completely in tabular form, but one typical set of data is given for purposes of illustration. Table I shows how the choices of photofinisher, A, differ from the

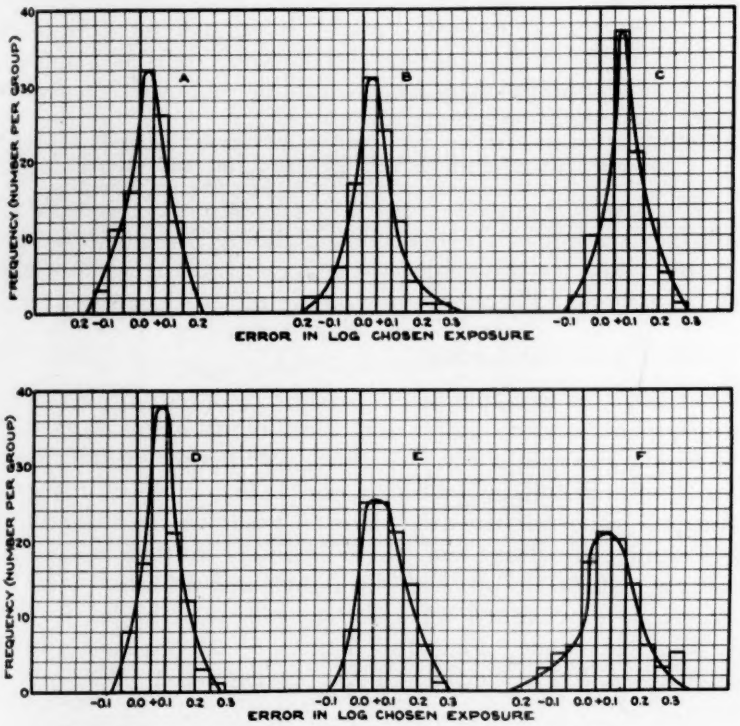
TABLE I.

Error (log E).....	$+0.1 \rightarrow +0.15$	$+0.05 \rightarrow +0.1$	$0.0 \rightarrow +0.05$
Number chosen.....	12	26	32
Error (log E).....	$0.0 \rightarrow -0.05$	$-0.05 \rightarrow -0.1$	$-0.1 \rightarrow -0.15$
Number chosen.....	16	11	3

average amateur choice in printing exposure. The results are expressed logarithmically and are grouped to show the number

and amount of the "errors" made by the photofinisher assuming that his hypothetical customer, the "average amateur," is correct. Thus the first figure in the second line designates the number of cases in which A would have given an exposure somewhere in the range between 0.1 and 0.15 greater than that required for the correct print. The next figure designates the number which A would have overprinted by an amount between 0.05 and 0.1.

FIG. 2.



Curves representing the exposure choice of professionals compared to amateurs.

Such data may be effectively presented as choice-frequency diagrams and this has been done in Fig. 2 for all six professional finishers. These diagrams illustrate graphically the number and size of the deviations of professional exposure assignments from the average value assigned by the amateur, a value represented by the straight vertical line at 0.0.

The relative merits of the various professionals can be evaluated at least qualitatively by a superficial inspection of these diagrams. The best photofinisher must be the one whose modal group lies nearest to the average amateur choice and whose curve shows the least deviation from this value. The arrangement followed in the figure probably represents a fair estimate of the order of abilities of the six men. A is the best with a maximum close to the amateur choice and a small deviation. F is the worst because it shows the broadest distribution.

It is interesting to note that the modal groups in all cases lie to the right of the amateur choice which may signify that, in general, photofinishers have a tendency to deliver darker prints than their customers want.

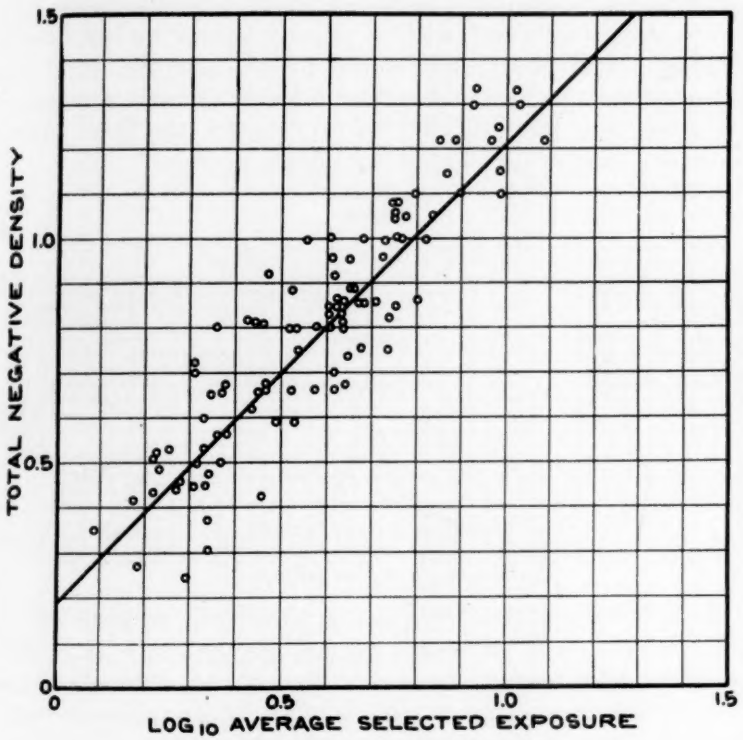
NEGATIVE MEASUREMENTS AND AVERAGE AMATEUR CHOICE.

The various possible objective measurement criteria of printing exposure can be tested in a manner very similar to that just discussed for the subjective judgment of the professional photofinishers. There are three purely physical measurements of negative density $\left(\log_{10} \frac{\text{incident intensity}}{\text{transmitted intensity}} \right)$ which may either singly or in combination serve to designate the required printing exposure. Determinations of maximum density (highlight density of the negative), minimum density (negative shadow density), and total density ($\log_{10}$ reciprocal of total transmission of picture area) may be made without the aid of any human direction, and, therefore, they may be used in an entirely automatic process. Maxima and minima could, of course, be determined by a scanning device similar to that used in television. The total density of the negative can be determined by collecting all the transmitted light into a photocell.

In these experiments it was not thought necessary to set up a scanning system for it was much simpler to determine the shadow and highlight densities with a visual densitometer. The photometric field of the densitometer for these measurements was limited to include in each case an area less than 1/1000 of the total negative area. Total density determinations were found by collecting all the transmitted light with a photometric integrator.

The correlation between each measurement and the corresponding average chosen printing exposure may be analyzed graphically. In Fig. 3, for example, are the data for total

FIG. 3.



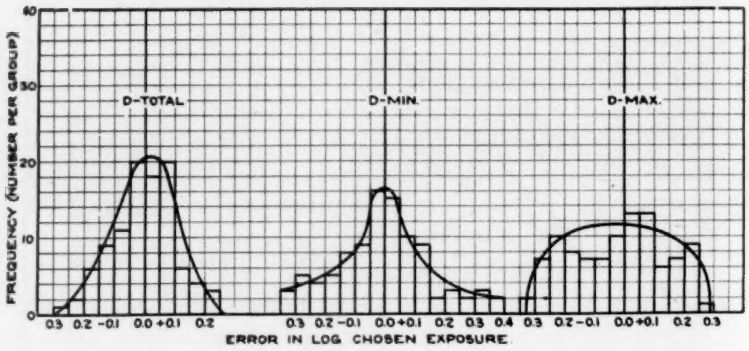
Distribution of total density *vs.* required exposure.

negative densities, plotted against the logarithm of the chosen exposure. The position and slope of the straight line was computed for all the data by the method of least squares. The slope of the log E/total D curve is unity within the error of determination, which signifies that the required exposure is inversely proportional to total negative transmission. This line may be regarded as the best calibration curve of an automatic printer which, by means of a total density determination, sets the printing exposure for the negative. The other

two density values of course may be treated in the same manner.

Diagrams exactly analogous to those shown for the professional printing errors may be drawn for automatic printers operating from each of the three density measurements. Referring to Fig. 3, points lying to the right of the straight line signify negatives which will be printed lighter by automatic judgment than the value desired by the average amateur. When the data are totaled for the different positive and negative errors and the data divided into ranges, the three error-frequency diagrams of Fig. 4 are found.

FIG. 4.



Curves representing exposure assignment by objective measurement compared to average amateur choice.

These distribution curves show that the total density is the best of the three objective criteria of printing exposure—minimum density is second best, while the maximum density measurement is almost valueless.

A comparative rating of each individual photofinisher's judgment and each negative density criterion of printing exposure may be made from the error frequency curves of Figs. 2 and 4, although without data regarding the "badness" of exposure errors, such a rating appears somewhat arbitrary.

Computation of the data in the amateur groups gives a value of 0.067 (log E units) for the probable error of the single observation relative to the average. The standard deviation (σ) is approximately 0.1. Without attempting to justify the

classification, one may assume that prints which do not exceed the amateur standard deviation are "good"; those which do not exceed $\pm 2\sigma$ are "passable"; and those which do exceed $\pm 2\sigma$ are "unsatisfactory."

The comparison of the merits of the six professionals and the density criteria in assigning printing exposure is given in Table II.

TABLE II.

	Number of Prints Out of 100 Classified as:		
	Good (Error less than σ).	Not Good but Passable (Error less than 2σ).	Unsatisfactory (Error in excess of 2σ).
Photofinisher A	85	15	
" B	78	20	2
* D_{total} criterion	69	25	6
Photofinisher C	60	34	6
" D	63	33	4
" E	58	35	8
" F	50	36	14
* $D_{min.}$ criterion	50	24	26
* $D_{max.}$ criteria	43	28	29

* Choice data of five observers with the large group of 500 negatives treated in the same manner check within a few per cent. the values reported here for the smaller group of negatives observed by the large group of amateurs.

For some purposes the foregoing mass treatment of the choice data is not entirely satisfactory. It is not complete in that it does not supply definite values for the amateur tolerance in printing exposure. It is not wholly convincing because there is a possibility that for some prints the tolerance is great and for others little. It might be that one picture would be satisfactory to the average amateur if it received twice as much exposure as that assigned by the average choice, while another picture might fail if it received only ten per cent. more.

The results of the mass treatment given in the table place the total density criterion better than the judgment of four reputedly excellent photofinishers. An inspection of the pictures as individuals rather than as a mass of statistics might give results less favorable to the measurement and more favorable to the individual finishers. The greater number of close approximations to amateur choice shown by the total density

criterion (69 less than σ) as compared with minimum density (50) and maximum density (43) singles out the former value as the best physical measurement. The last two criteria are therefore discarded at this point.

To supply the missing information on printing exposure tolerance, the medium paper prints which had been mounted as shown in Fig. 1 were cut apart, stacked together, and thoroughly shuffled. Again the amateur observers were asked to inspect the prints, but this time they were requested to judge each print on its own merits. They were asked to reject those prints with which they were not satisfied and keep only those prints which were neither too dark nor too light. The observers were thus put in the same position as a customer who received a set of prints from his photofinisher. That each print was actually judged on its own merits, and not in comparison with lighter and darker prints from the same negative, was assured by sorting to prevent juxtaposition of two like prints. This second judging experiment was carried out several months after the first so there is little likelihood that memory could have influenced the results.

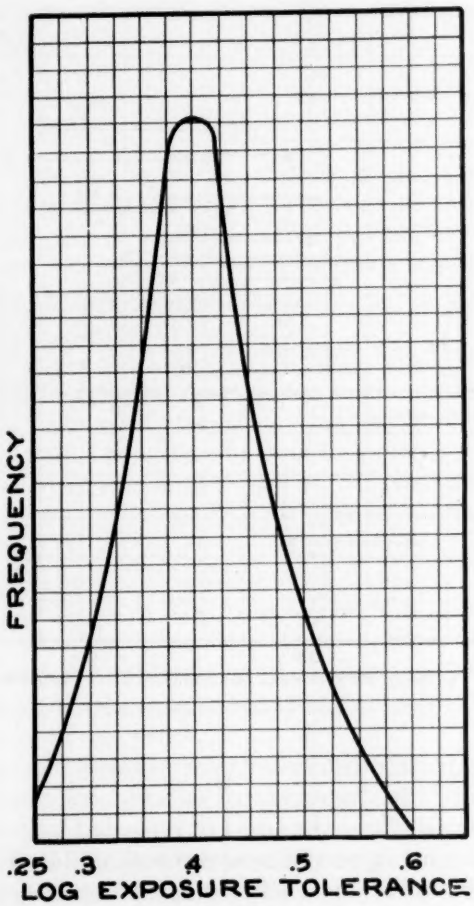
For each picture, the arithmetical mean exposure of the rejected dark print was found. From this value one half step (0.075 log E) was subtracted to find the greatest tolerable value. The least tolerable value was found by adding one half step to the average for the light print rejections. This procedure in fixing the tolerance limits arbitrarily places the boundary print midway between a definitely accepted and a definitely rejected print.

The tolerance data show distinctly that there is a difference between the allowable errors for different pictures. The least tolerance range or difference between darkest and lightest tolerable printing exposures was 0.25 and the greatest was 0.6. The majority of negatives have a tolerance of 0.4. These facts are mentioned for emphasis though they may be seen at a glance from the exposure tolerance frequency distribution curve in Fig. 5.

The exposure tolerance of a print may obviously be represented in a graph by a line parallel to the exposure axis. As an example, values for a few of the pictures are plotted in this manner against total density in Fig. 6. Length of the lines

shows the extent of the tolerance. Numbers at the ends of the lines are merely arbitrary negative numbers. The calibration curve of an automatic printer operating on the total density

FIG. 5.

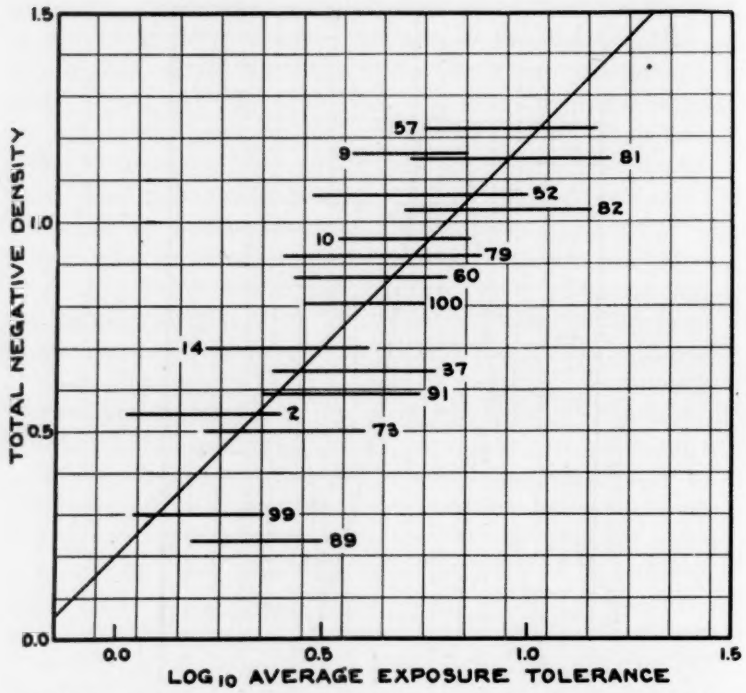


Curve showing distribution of exposure tolerance.

criterion taken from Fig. 3 is shown on this graph. If the horizontal line which indicates the exposure tolerance does not intersect the calibration curve, the print produced by the automatic printer will lie outside of the tolerance as, for example,

No. 89 which would be automatically printed lighter than the tolerance and No. 9 which would be printed heavier. A satisfactory print results when the line is intersected.

FIG. 6.



Total density vs. required exposure (tolerance in exposure indicated by length of lines).

The choice of the individual professionals may be graded in a like manner. If the exposure selected by the finisher lies inside of the tolerance, the print is regarded as passable.

Results according to this new method of classification summarized in Table III now show the human judgments in all cases to be slightly better than the physical measurement. This change in rating is quite obviously a result of tolerance variation, a fact which is concealed in the treatment of the data purely as a mass of statistics. The relative merits of the individual finishers are essentially unchanged by the latter method of classification.

TABLE III.

Exposure Assigned by	Passable Prints	Unsatisfactory Prints
Photofinisher A	100	0
" B	98	2
" C	97	3
" D	97	3
" E	96	4
" F	95	5
D_{total} criterion	94	6

It is reasonable to pause at this point to consider the consequences of the data which have been presented thus far. An automatic printer which sets the printing exposure from a measurement of the total negative density cannot equal the judgment of an experienced expert when the expert delivers the best results of which he is capable. But, before the expert can deliver these results which give him a rating of 95 to 100 in customer satisfaction, he must produce his prints (from negatives). Not only must he make the decision of whether a given print should be delivered but he must decide from the negative how to produce this print. To the prints which he loses because of error in the first decision must be added prints lost because of errors which he makes in guessing the correct exposure. Fairly reliable data about professional printing losses are available in the cost accounting records of the photofinishers. Printing room losses are seldom less than five per cent. and frequently as great as ten per cent. Photoelectric exposure assignment should therefore compare favorably with expert judgment.

An automatic printer aided by some human judgment is an alternative which might be worth consideration if it can raise the percentage of success to some value between 94 and 100 per cent. One possibility in this direction is to pick out failure-type negatives prior to printing. It has been observed, for instance, that most of the negatives which are overprinted on the basis of an average density measurement are pictures containing an abnormal amount of sky or sky and water. If an auxiliary, manually operated, control is provided to give such scenes fifty per cent. less than their photoelectrically assigned exposure, the resulting prints will usually fall within

the exposure tolerance range. For example, referring to Fig. 6, negative No. 9 if given fifty per cent. less exposure (about 0.2 in logarithm units) would receive an exposure within the tolerated value.

Manual control of print development, as is practiced at present, will save prints which are over- or underexposed by as much as fifty per cent. without having any detrimental effect upon the quality of the finished prints.

Combining these two procedures—allowance for subject failure and inspection development—would probably raise the percentage of passable prints above 99. It is to be remembered, however, that the use of either of these humanly controlled makeshifts will entail some loss of the speed with which an entirely automatic process with fixed development can operate.

PAPER GRADE CONTROL.

The procedure adopted in the analysis of exposure assignment was, first, to find what the amateur public wants, second, to find what the professional finisher gives him, and third, to compare this result with what he would receive if photoelectric measurement were substituted for human judgment.

A similar procedure may be followed to analyze the results of paper grade choice though in this case the findings are not so readily described. Exposure can be expressed as a number and a group of chosen exposures can be expressed as the arithmetical average. Paper characteristics cannot be expressed as a single number and the designation of a chosen average characteristic is by no means a simple matter.

The tabulated data which show the grade of paper preferred by each of the eleven amateurs for each of the hundred negatives may, however, be directly compared with the choices of each of the professionals with interesting and revealing results. As an example, the eleven paper grade choices for a single negative may be distributed thus: 4 contrast, 5 medium, 2 normal. If professional A selects medium paper he wins five choices and loses six. When dealing with a spread of amateur opinion, the professional cannot, of course, rate 100 per cent. upon this grading basis.

A few general remarks concerning the variation in amateur opinion will help to explain Table IV, which gives the relative

standing of the six professionals in the accuracy of paper grade choice. Eleven hundred statistics are represented—eleven choices for each of the hundred negatives. Among the data there is no example of unanimous agreement. In seventy-one instances all three papers are chosen; in the remaining twenty-nine the choice is concentrated between two grades. The medium paper is chosen by at least four observers in every case, and in ninety-one cases by a plurality. If the paper which satisfies the greatest number in each case could be supplied by some perfect photofinisher or by some perfect negative measuring method, *sixty-two* per cent. of the customers would be satisfied. If medium paper is supplied arbitrarily for all negatives *sixty* per cent. of the customers would be satisfied. No one of the professional photofinishers equals these percentages by the exercise of his own choice among the three grades.

The actual ratings are given in Table IV.

TABLE IV.

Table Comparing Paper Grade Choice of Six Professionals and Eleven Amateurs.

Finisher	Coincidental Choices	Percentage $\left(\frac{\text{coincidence} \times 100}{1100}\right)$
D	607	55
B	551	50
C	549	50
E	528	48
A	515	47
F	509	46
Arbitrary use of M paper	663	60
Best possible result using all papers	684	62

For the inventor, there is a glaringly definite conclusion to be drawn from this table of data. A complicated photoelectric method of choosing the paper grade from negative measurements is not worth while because it can only hope to raise the percentage of success by two per cent. over that possible by using the single grade of paper which best suits the average. Proof is available for this statement only for the restricted conditions of this experiment—namely, the single

negative emulsion type and the controlled development of all negatives.

The strong statistical evidence that a single paper grade will give satisfactory results with controlled negative development leads one to inquire into the question of paper grade from the point of view of classical tone reproduction theory. This theory states in essence that the positive gradient (dD/d log E) should be reciprocally related to the negative gradient.

A knowledge of the photographic characteristic curve of the average negative of this experiment and of the characteristics of the positive materials used is therefore pertinent to this study.

THE NEGATIVE AND POSITIVE CHARACTERISTICS.

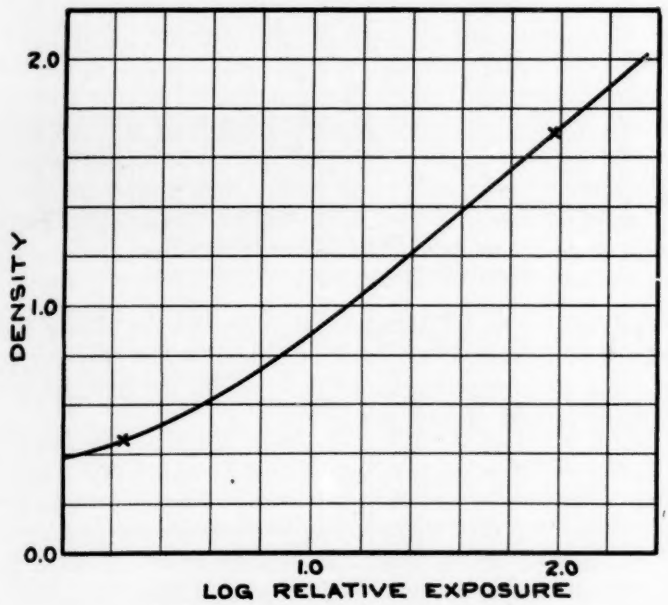
The production of negative density in a camera proceeds according to the characteristic curve of the emulsion, the slope of which depends upon the degree of negative development. In photographic research as it is ordinarily applied to the analysis of emulsion characteristics, the properties of a given emulsion under a given set of conditions are studied by exposing a sample of the emulsion in a sensitometer to a constant intensity for a varying time. For certain reasons, notably the failure of the reciprocity law and the presence of nonimage-forming light in a camera, data obtained in a sensitometer may not be directly applicable to the study of tone reproduction through the steps of image formation in the camera.

Data which are directly applicable may be obtained by using the camera as a sensitometer, by photographing a test object containing a series of areas of known brightness. The result of such a test for the conditions applying to the exposure and development of the test negatives for this experiment is shown in Fig. 7.

The mean highlight and shadow densities of the 100 negatives involved in the test are 1.7 and 0.46, respectively. These points are designated by crosses on the negative characteristic curve (Fig. 7); thus the region of the curve lying between the crosses may in a statistical sense be regarded as the typical negative of this experiment.

The characteristics of the three papers used in this experiment are shown in Fig. 8. These curves are typical of all photographic papers in the manner in which the density/log E gradient varies. The low density (toe) region is characterized by an increasing gradient; at higher densities the gradient becomes constant for some distance, at high densities it decreases. The shapes of these curves are not ideal from the point of view of tone reproduction theory.

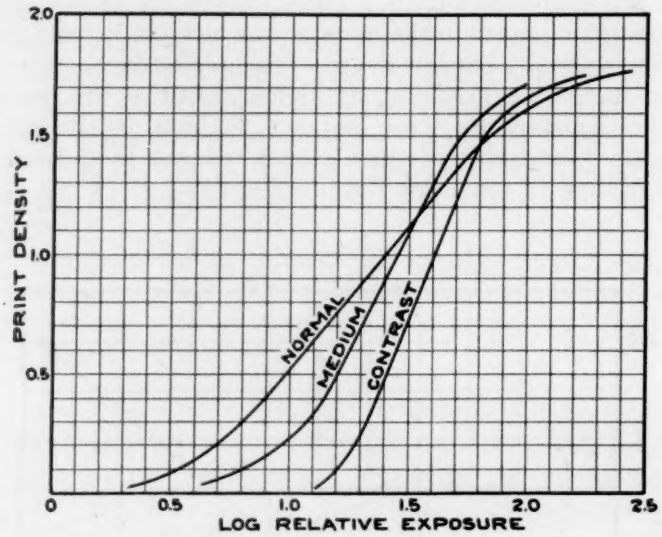
FIG. 7.



Average negative optical image characteristic curve.

The nearest fit of actual paper to the ideal is probably to be found in the one whose average gradient is the closest to the average gradient of the ideal paper. The average gradient of the ideal curve would be the reciprocal of the average gradient of the typical negative and this value is found to be 1.6. Average gradients for the three curves in Fig. 8 are 1.3, 1.7, and 2.0. The medium paper with a gradient of 1.7 is slightly higher in contrast than the ideal but fits closer than

FIG. 8.



Actual characteristics of papers used in experiment.

either of the others. This conclusion checks the choice statistics nicely in a qualitative way. Choices of the two groups of observers are summarized in Table V where the percentages of these three papers chosen are listed.

TABLE V.

Group	Chosen prints on		
	Contrast	Medium	Normal
Professional	17	64	19
Amateur	16	60	24

Statistically, a paper close to the medium but with a slight leaning toward a softer material is indicated.

THE WEAKNESS IN THE SINGLE PAPER GRADE IDEA.

There seems to be no fallacy in the reasoning which leads to the conclusion that prospective customers would be well satisfied with a single grade of paper of the correct or nearly correct

characteristics. But there is a psychological stumbling block in the way of commercial application of the single grade idea even with controlled negative development.

The actual customer for an automatic printer is the photofinishing expert and not the amateur to whom the prints are sold. The photofinisher knows that he has always had to do two things to make a print—choose the proper exposure and select the proper paper. He will be satisfied with the photoelectric exposure selection because it will be within his tolerance. He may not be entirely satisfied with a single grade of paper because, according to the statistics, he will be contented only about sixty-odd per cent. of the time. By personal selection among three or more grades of paper he can satisfy himself one hundred per cent. of the time. He compares this personal one hundred per cent. satisfaction with the personal sixty-odd per cent. satisfaction to the detriment of the single grade of paper idea. It will be hard to convince him that what pleases him all the time may please his customers only about fifty per cent. of the time. In view of this psychological difficulty it would be of some value if it were possible to devise a photoelectric device which would select paper grades successfully enough to pass with the photofinishers and a brief study of this matter follows.

The choice data of the professional group show slightly greater consistency than the data of the amateur group. Among the hundred negatives there are eighty-eight instances where a preference in grade of paper is indicated by a plurality of professional votes. Eight of these indicated preferences are for normal, seven for contrast, and seventy-three for medium paper. An ideal photoelectric selection to suit the average professional would shift papers whenever the plurality shifted.

Unfortunately, the objectively measurable negative characteristics show very little correlation with the most popular grade of paper. The two quantities which might be expected to have some bearing upon the grade of paper are negative contrast ($D_{max.} - D_{min.}$) or total density. A high contrast paper should, in general, be used for a low contrast negative. Low contrast negatives are frequently those of low total density. Both criteria, however, appear to be worthless. To operate successfully as a selector of paper, the negative con-

trast range (or total density range) for one grade of paper must be distinct from that for the next harder and softer grades. The ranges given by these data overlap each other for all three grades.

There is an indication among some as yet incomplete experiments that when dealing with negatives of varying degrees of development, there is a more positive paper grade choice than is reported here and a slightly better correlation of the suggested criteria. From these data it appears that a photoelectric paper selector which shifts from a medium to a contrast paper for negatives below 0.4 in average density would be about seventy-five per cent. successful. It is almost certain that such a device would at worst do no harm and even with controlled development negatives it might have a psychological advantage.

THE COMMERCIAL APPLICATION OF AN AUTOMATIC PRINTING SYSTEM.

For automatic printing to be a complete success in a commercial photofinishing plant, it would be necessary to make some changes in the technic employed in present establishments. Closer negative development control than is now practiced is the first desirable improvement. It is desirable not only from the point of view that the number of paper grades required for printing are reduced, but closer control is certain to bring about an improvement in the average negative quality and to reduce the number of failure negatives. A single type of negative emulsion would simplify both development and printing but this, of course, is not feasible under present commercial conditions. Even with a number of emulsion types, if standardized development is followed, it should be possible by trial to fit any negative characteristic with an appropriate grade of paper.

The magnitude of the advantages of automatized photofinishing over the present manually operated system naturally depends largely upon the cleverness of the inventions which are developed. It is not the purpose of this paper to discuss specific developments, but rather to point out the possibilities in the field. To summarize the situation it appears:

1. That printing exposure control by photoelectric measurement is possible and that the waste of an automatic printer

will be no more and possibly less than that of an expert manual operator.

2. That with controlled negative development the use of a single grade of paper will not result in many errors which are beyond the amateur tolerance.

3. That an unskilled operator of an automatic printer might work at a speed greater than that of the present expert. The top speed of an automatic printer would be dependent almost entirely upon the devices employed to feed the negatives and paper and only slightly upon the manual dexterity of the operator.

4. That because of using less highly trained labor the seasonal nature of the photofinishing business would become less of a business handicap.

February 1937.

Synchronized Beacons Mark World's Greatest Bridge.—P. B. GARRETT (*The Electric Journal*, Vol. 34, No. 7). Night time travelers of the air have no difficulty in quickly identifying the topmost tower elevations of the mighty San Francisco-Oakland Bay bridge. Among the myriads of white and colored lights that dot the world's largest land-locked harbor there stands out in bold relief a line of six 24 inch rotating beacons. Conforming with all requirements of the Department of Commerce, the rotating beacons are equipped with parabolic silvered glass reflectors, 1000-watt, 32-volt lamps, and red lenses. Standing 53 inches high, they each produce 8,000,000 candle-power. The rotation of these beacons is synchronized to provide a unique identification. A central operator several miles distant from the beacon locations has before him a control board on which is a miniature replica of the complete bridge. The operating condition of each beacon is continuously and automatically portrayed thereon.

R. H. O.

1250 KV. Generator for Cavendish Laboratory.—(*Engineering*, Vol. CXLIV, No. 3730.) This Cambridge, England, laboratory has recently been supplied with a generator capable of producing continuous voltage. It is to be distinguished from an impulse generator, which can only deliver the full power at intervals which last some millionths of a second. The equipment is of the cascade type, in which the well known principle of voltage multiplication through several stages by means of valves and condensers is employed. To ensure the necessary low voltage drop and small heating energy of the filament in the high tension rectifier, gas filled rectifying valves are used. The filaments of these valves are heated by a small high frequency generator, which passes current through the series of high tension condensers and also through small coils which are arranged between and in series with the condensers. The output of the generator is 5 KW., i.e. 4 milliamperes at a constant tension of 1250 KV. and there are 12 stages which operate at a frequency of 200 cycles. The voltage drop of the plant is 40 KV. at 2 milliamperes. The equipment is to be used for the experimental work on transmutation.

R. H. O.

A STUDY OF BLEACH CLAY SOLUBILITY.

BY

P. G. NUTTING.*

ABSTRACT.

The five varieties of bleach clays indicated by leach and bleach tests are all dominantly montmorillonite and are not readily distinguishable by X-ray tests, petrography, by chemical analyses or thermal dehydration curves. Active clays yield a higher percentage of silica in water solution than inactive clays. In dilute hydrochloric acid all clays have a high maximum solubility of silica at a dilution of about 0.5 liter of water per gram of clay and acid. In dilute sodium carbonate solution there is a maximum solubility of silica at about 5 liters of water per gram of clay and of sodium carbonate. Optimum bleach is attained by removal of about 2/3 of the bases. Bentonites are converted to fuller's earths by a slow leach in very dilute or weak acids. Applications of these results to the activation of bleach clays, to the soil problem of plant food and to the chemical problem of the solubility of silica are indicated.

Many curious technical, agricultural and geologic problems are related to the solubility and hydration of silica and silicates in water and water solutions; the degradation and regeneration of soils, the alteration of tuff to bentonite with the further alteration of the latter to bleach clay, the ascent of soil solutions in growing plants and the constitution of natural waters may be mentioned as typical. In a preliminary study of the solution of minerals in water [1] it was noted that the addition of a trace of acid to the water greatly increases the solubility of the silica of clays and soils. This paper is a report of further work in that field covering a wide range of acid concentrations and dilute alkalies and is part of a general program of research on the interrelations of silica (and silicates), water (and water solutions) and oil.

The bleach clays (bentonites and fuller's earths) were chosen for study because of their mineralogic homogeneity. Being bentonites derived from glassy igneous materials (tuffs), they are not (like ordinary clays) merely aggregates of diverse

* Published by permission of the Director, U. S. Geological Survey.

[1] "The Solution and Colloidal Dispersion of Minerals in Water." P. G. Nutting, *J. Wash. Acad. of Sci.*, May 19, 1932, p. 266.

mineral crystals. The bleach clays consist essentially of the hydrous alumino-silicate mineral montmorillonite, a clay mineral of especial interest for its varied and powerful adsorptive properties under varied surface conditions. This material is also similar in chemical composition and mineralogical character to the essential clay mineral of many soils. The action of acid solutions on such clays is complicated both by the adsorption of anions and by the hydrolysis of the salts formed and of the silica set free. Strong acid chiefly affects the bases, leaving the silica in solid form while very dilute acids take both silica and bases into solution. The high maxima for more dilute alkali solutions should be of profound significance in soil chemistry and in geochemistry. The involved nature of the action of reagents necessitated a rather extended investigation in four series of tests as follows:

I. Acid concentrations (0.3–9N) and times of digestion (0.5–5.0 hours) were varied while the amounts of clay and the volume of solvent were held constant. The per cent. loss in weight of clay and the decolorizing power of each batch were determined. This series shows the optimum leach of each clay as regards bleaching power as well as the nature of the attack by acid.

II. Clay and water (both in excess) and time of digestion were held constant while the added acid was varied through a range of extreme dilution. This series includes natural conditions in clay beds. Dissolved silica and bases were determined.

III. Concentration of dilute acid (0.2N), amount of solvent (1 liter) and time of digestion held constant while the amount of clay was varied from very little up to a mud. Clay dispersed in lakes and settled on their bottoms is subject to such conditions. Dissolved silica was determined.

IV. Equal amounts (1 gram) of clay and acid or alkali with water varied in amount over a wide range. Dissolved silica was determined.

The clays studied were the following:

1. Sanders. A white bentonite from northeastern Arizona supplied by the Filtrol Co., Los Angeles. Yields

readily to acid. The chief source of activated clay in America.

2. Westcliffe. A pink bentonite from a large deposit near Silver Cliff, Colorado. An average bentonite, fairly tough chemically.
3. Marianna. From 1.4 miles west of Marianna, Florida. This bleaches, when untreated, like a good fuller's earth yet activates to as high bleaching power as any bentonite.
4. Quincy. A selected sample of the best fuller's earth mined by the Floridan Company. Submitted by them. Acid leaching lowers bleaching power.
5. New Mexico. A "pure montmorillonite" from north central New Mexico. Pinkish gray, waxy. Yields too readily to acid for a good bleach clay.
6. Wyoming. Typical greenish gray swelling bentonite, only slightly activable. Commercial "Volclay," Am. Colloid Co.
7. Tonsil. A commercial activated bentonite of high quality from Bavaria.

Of these, the first four were studied with strong acids, all seven with dilute acids. Nos. 1, 2, 3, and 5 were analyzed by J. G. Fairchild of the Geological Survey staff from the same stock (150 mesh, room dried) used in the acid leach and thermal dehydration tests, with the results shown in Table 1.

TABLE 1.
Analyses of Bentonites.

	1	2	3	5	M	B
SiO_2	51.20	55.59	55.40	52.30	50.73	50.87
Al_2O_3	15.12	14.86	23.68	14.43	17.22	28.78
Fe_2O_3	1.41	1.23	3.76	2.00	—	—
MgO	5.22	4.30	1.09	6.15	4.54	—
CaO	2.71	2.26	.05	2.12	3.16	—
Na_2O	.50	.42	.02	.50	—	—
K_2O	.08	.28	1.75	.52	—	—
H_2O-	16.78	14.23	5.50	15.78	24.35	20.35
H_2O+	6.92	7.12	8.00	6.35		
TiO_2	.10	.06	.78	.20	—	—
P_2O_5	—	.02	.04	.02	—	—
MnO	.03	.15	.01	.05	—	—
	100.07	100.52	100.08	100.62	100.00	100.00

A number of analyses of Nos. 4 and 6 are available showing essentially the same composition as 1, 2, and 5, namely, that of montmorillonite. Marianna (No. 3) is more like beidellite in composition.

The column headed "M" is the composition of montmorillonite satisfying the formula (Mg, Ca) $O \cdot Al_2O_3 \cdot 5SiO_2 \cdot 8H_2O$ with $MgO : CaO = 2 : 1$. Column "B" is $Al_2O_3 \cdot 3SiO_2 \cdot 4H_2O$. Many analyses of bentonites are given by Ross and Shannon.[2] Analyses Nos. 1, 2 and 5 are seen to correspond closely with "M," and No. 3 with "B." The dehydration curve for No. 3 (Fig. 16), with its pronounced cliff at 500°, also indicates that it is chiefly beidellite.

I. LEACH AND BLEACH TESTS OF FOUR CLAYS.

In this series a constant amount (3.5 grams) of ground, room-dry clay was digested in a fixed quantity of acid (100 cc. HCl 0.3, 0.6, 1.2, 3, 6, and 9N) at 94° C. for 0.5, 1, 2, 3.5, and 5 hours, then washed, dried, weighed and tested for bleaching power. Such a series of tests shows the concentration of acid and time of cook which will give optimum decolorizing power for a given clay and oil.

The acid leach data are summarized in the four sets of curves (Figs. 1 to 4) for Sanders and Westcliffe bentonites, Quincy fuller's earth and Marianna clay which is both active and further activable. In each case the per cent. loss in weight (including water not in equilibrium with room humidity) is plotted against time of cook at 94° C. in hours at each of the six acid concentrations.

In the more dilute acids the small amount of dissolved material is chiefly silica, calcium, magnesium and potassium. Blanks run with distilled water showed less than 0.3 per cent. dissolved hence only a negligible amount of free soluble salt is present in these clays. Iron usually yields readily only to the stronger acids. The maximum leach varies from 38 to 42 per cent. The maximum rate of leach is for 6N acid (20 per cent.) between 1 and 1.5 hours.

Marked differences in the leachibility of these clays may be noted. While Quincy yields readily to dilute acid, the curves for different concentrations run nearly parallel indi-

[2] *Jour. Am. Ceramic Soc.*, 9, 77–96, Feb. 1928.

FIG. 1.

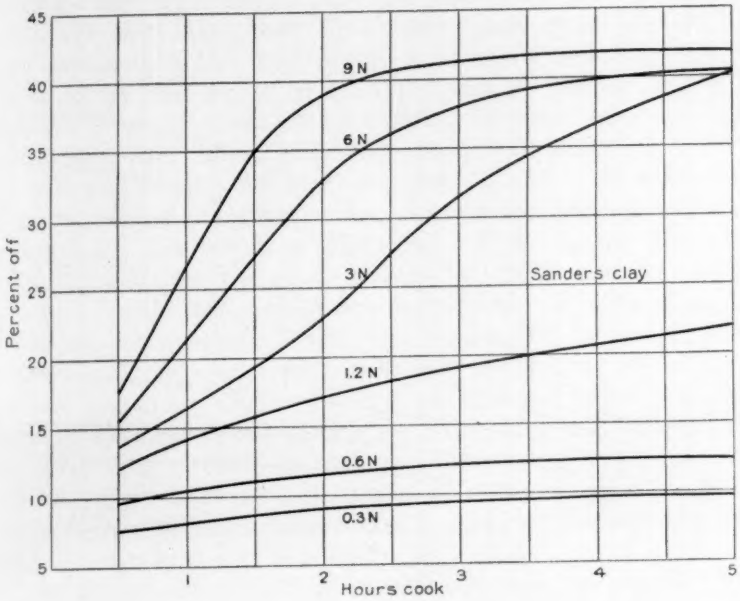

9 N
6 N
3 N
1.2 N
0.6 N
0.3 N
Sanders clay
Percent off
Hours cook
45
40
35
30
25
20
15
10
5
1
2
3
4
5

FIG. 2.

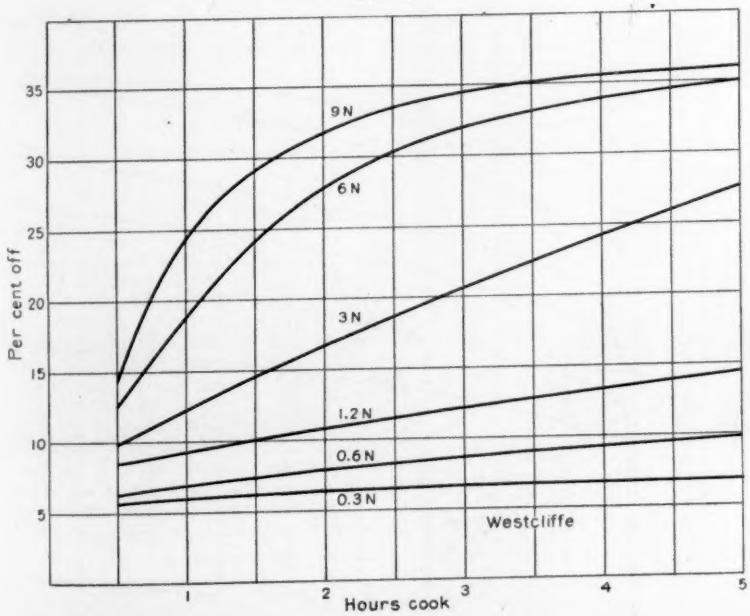

9 N
6 N
3 N
1.2 N
0.6 N
0.3 N
Westcliffe
Per cent off
Hours cook
35
30
25
20
15
10
5
1
2
3
4
5

FIG. 3.

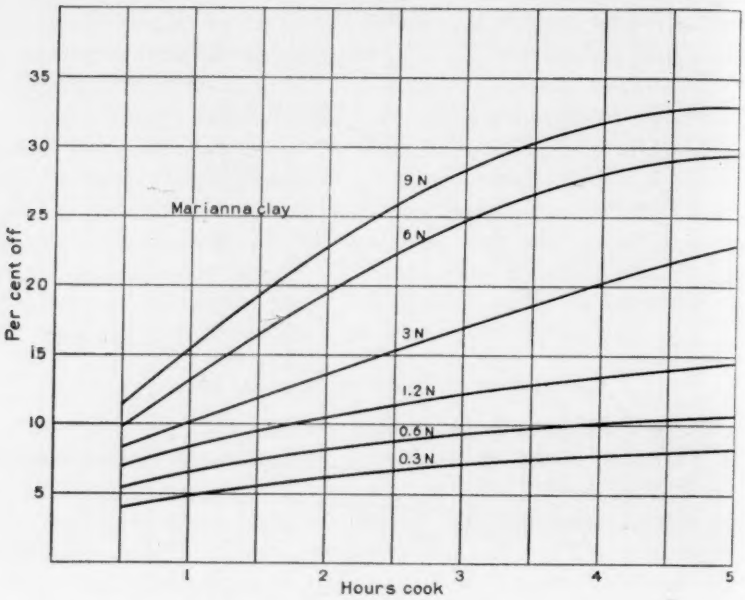
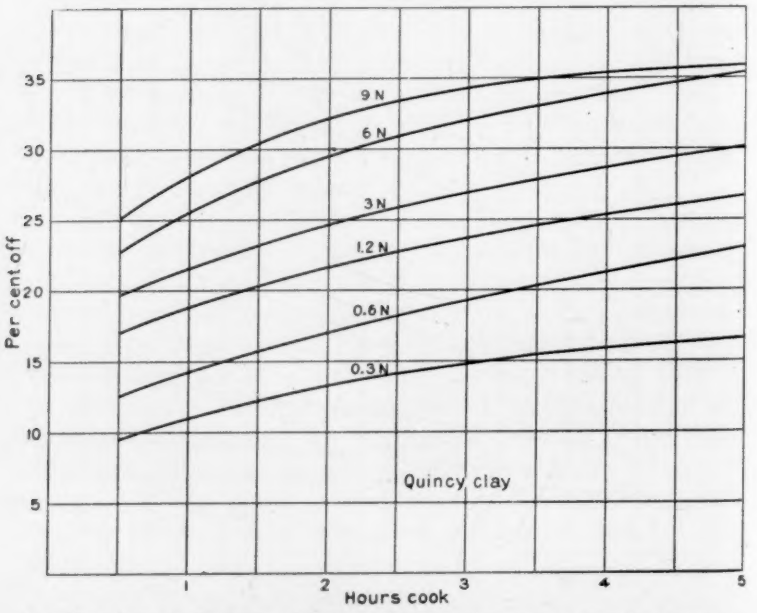


FIG. 4.



Leaching of Sanders, Westcliffe, Quincy and Marianna clays vs. acid concentration and time of digestion.

cating that strong and weak acids react in a similar manner. with the bentonites, curvatures are much more marked for the stronger acids, indicating a different reaction. It is noteworthy that the fuller's earth (Quincy), though probably derived from a bentonite by leaching in weak acid with loss of further activability, still yields readily to acid.

Bleach Tests. Each of the thirty leaches of each clay sample was tested for bleaching power by the writer's method [3] using crude petroleum as a test oil. This method gives far more detail than the usual refinery methods using cylinder stock. The bleach ratings are the volumes of percolating oil bleached water-white to the first appearance of green (wh), yellow (gr), red (yel) and black (red) divided by the volume of the bleaching clay. Instead of plotting bleach against each of the four variables concentration of acid, ratio of acid to clay, time of cook and temperature of cook, it is plotted against percentage loss of weight of clay during acid treatment [3] since this has been found a satisfactory way of combining the four separate effects.

In Fig. 5 are plotted all the bleach tests for the Sanders clay for all concentrations of acid (0.3 to 9N) and times of cook (0.5 to 5 hours). Cooking in 0.3N acid added nothing to the decolorizing action of raw clay (0.4–0.5) even though

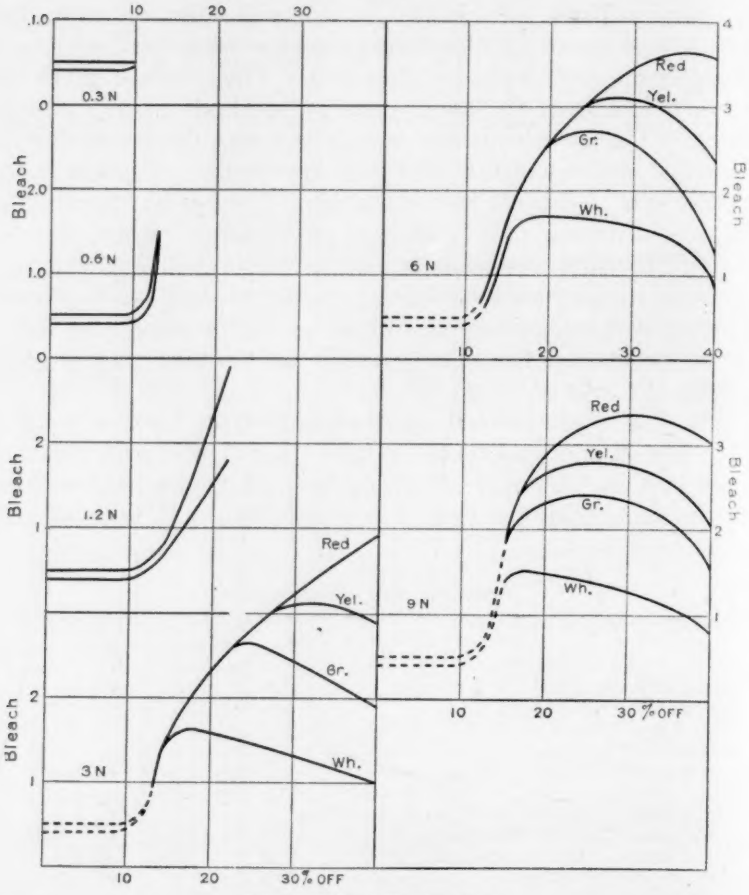
TABLE 2.
Leach and Bleach Test Results.

	Sanders	Westcliffe	Quincy	Marianna
Maximum leach, 6N HCl (% of clay)	41.8	36.0	36.0	33.0
Maximum leach, 0.3N HCl	9.6	6.9	16.5	8.0
Leach 2 hrs., 6N acid, 94° C.	33.0	28.1	29.5	19.6
Rate of leach, 1–1.5 hrs., in %/hr., 0.3N	1.0	0.5	2.7	1.5
Rate of leach, 1–1.5 hrs., in %/hr., 0.6	1.1	1.0	2.7	1.7
Rate of leach, 1–1.5 hrs., in %/hr., 1.2	2.5	1.6	3.3	2.1
Rate of leach, 1–1.5 hrs., in %/hr., 3.0	5.5	4.5	4.2	3.8
Rate of leach, 1–1.5 hrs., in %/hr., 6.0	11.8	12.3	4.5	6.4
Rate of leach, 1–1.5 hrs., in %/hr., 9.0	18.4	9.2	4.6	7.7
Leach for first activation	12.5	10.0	(20–)	13.7 (3N)
Leach for best water-white bleach	20	24	0	20 (6N)
Best water-white bleach	1.6	1.5	1.1	1.3
Leach for best red bleach, % of clay	33	33	0	31
Best red bleach	3.6	3.6	1.9	3.5
Bleach fully leached, water-white	0.8	0.6	0.5	0.8
Bleach fully leached, red	3.1	3.4	1.8	3.5

[3] Nutting, *Oil and Gas Jour.*, Nov. 16, 1933.

the 5 hour leach was 9.6 per cent. The 5 hour cook in 0.6N (2 per cent.) acid, removing 13 per cent. of the clay shows the first marked increase in bleaching power. In this cook the first iron appeared in solution. In the 1.2N cook, bleaching

FIG. 5.



Bleach vs. leach, Sanders clay.

action is well developed though color separation is not. The leaches in 3, 6 and 9N acid shows complete activation with but minor differences. The best water-white bleach (vegetable oils), 1.6, is attained when the leach is 18–20 per cent.

The best red bleach (mineral oil lubricants), 3.6, is attained by a leach of about 33 per cent. For this clay, which leaches readily in acid, the optimum bleach appears to be a 5 hour cook in 3N (10 per cent.) acid rather than the normal 2 hour cook in 20 per cent. acid.

The single sets of bleach curves for each clay cooked in 6N (20 per cent.) acid are shown in Figs. 6–9. Westcliffe is a normal bentonite in that iron is released gradually from the start while Sanders (which is almost snow white) holds to its iron until the leaching becomes drastic. The bleach curves for the Quincy fuller's earth differ widely from each other.

FIG. 6.

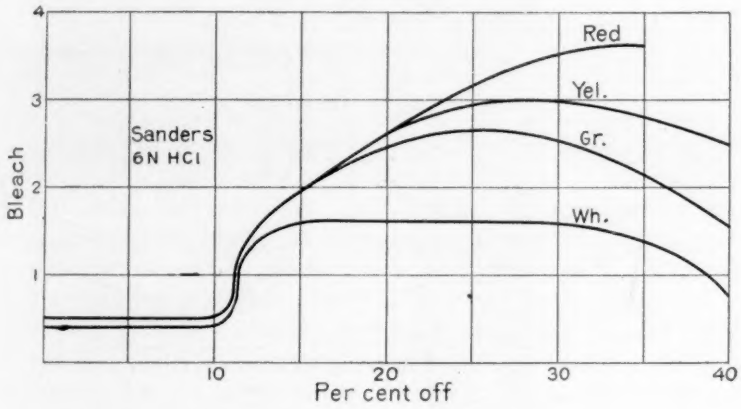


FIG. 7.

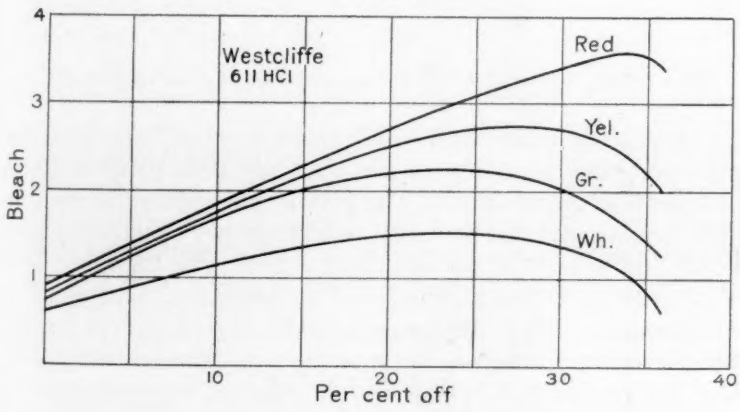


FIG. 8.

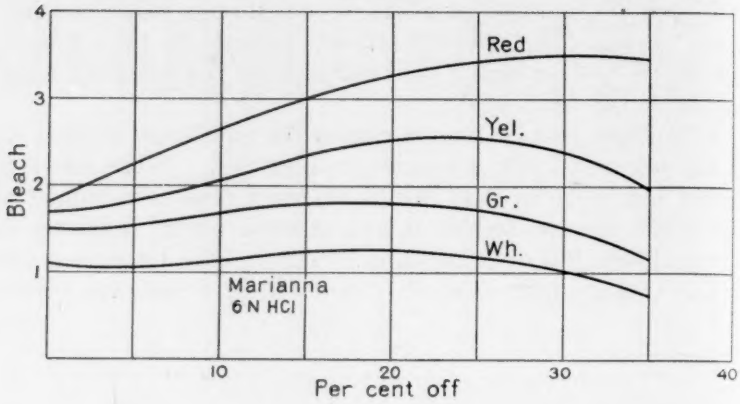
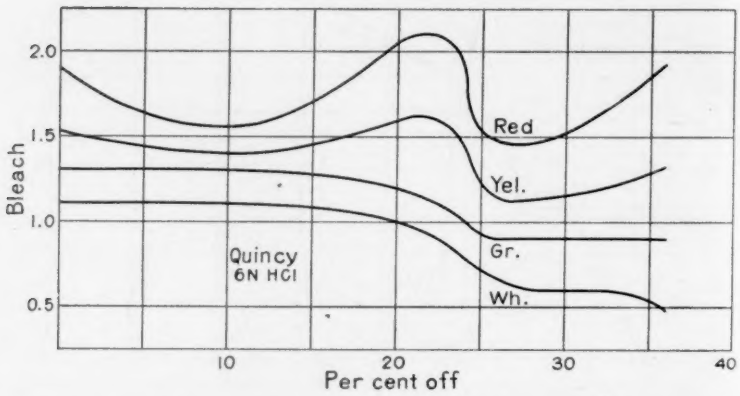


FIG. 9.



Bleach curves for Sanders, Quincy, Marianna and Westcliffe clays leached in 6N HCl.

The curves for water white and green are but little affected by leaching out to about 16 per cent. off, then drop to lower levels beyond 26 per cent. The yellow and red curves drop to a first minimum at 10 per cent., rise to 22 per cent., drop to a second minimum at 27 per cent., then rise again. This peculiar behavior may be related to molecular arrangement and appears worth further study. The bleach curves for the Marianna clay (which is both active and further activable) show the behavior of both fuller's earth and bentonite.

The acid attacking a bleach clay is never all used up even with insufficient acid (excess clay) and long continued digestion. For leaching to proceed, there must be sufficient free acid remaining in solution to over-balance the acid silica left openbonded by the loss of some of the bases. Further, as the experimental results show, longer cooking in a more dilute acid is *not* the equivalent of a shorter cook in stronger acid though the amount of bases removed be the same. Hence it pays to waste some acid even from the practical standpoint of the most bleaching power for the money. Some clays bleach mineral oils fairly well when the acid leach is pushed to the limit by long cooking, with limited acid, but the heat expense exceeds that of unused acid. Even with 1 per cent. (0.3N) acid less than half the acid is used up, and at higher concentrations, an even smaller fraction.

II. SOLUBILITY IN DILUTE ACIDS.

Many clays and soils which yield silica only slightly to either strong acids or pure water,[1] will yield it copiously to dilute acids and of course to alkalies. Dilute hydrochloric acid appears to serve as a cation acceptor, releasing the silica to dissolve as silicic acid in the water. Bentonite, glauconite and similar material, treated with 1 per cent. hydrochloric acid or with oxalic acid, gradually acquires the bleaching power of a fuller's earth but is not further activable [4] even by strong acids. Finally there are many curious effects of alternate moistening and drying on bentonites. Some are reduced to fuller's earths by this process alone.[5] Most bentonites, whether raw or acid-treated, lose activability rapidly on room drying, but fuller's earths improve slightly with dry storage. The most promising line of attack on these problems appeared to be a study of the solubility of bleach clays in dilute acids.

The program finally adopted was to make a 24 hour extract of the ground clay at 97–99° C. in 1000 cc. of acid solution of normalities 0, 0.03, 0.06, 0.12, 0.3, etc., then determine silica and total solids in the extract. From 3 to 12 grams of

[4] "Activation of Bleaching Clays": *Oil and Gas Jour.*, Nov. 16, 1933.

[5] "The Technical Basis of the Bleaching Clay Industry": *Bull. Am. Assoc. Pet. Geol.*, **19**, 1045, July 1935.

150 mesh clay (0.1 mm.), the amount being the same for each clay, was used in each test. Previous work on solubility had shown [1] that such an extract is very nearly saturated. The precision is not high but is ample to show the properties under investigation. Many interesting details appear well worth further study.

The extract was filtered through the clay itself on a filter paper. The best filter papers contain some pin holes and will pass some clay but if the first third of the filtrate passing through is returned, even a poor paper will give a filtrate showing no Tyndall beam. The last few hours of extraction were always at vigorously boiling temperatures and the extract was filtered boiling hot. It has been shown [1] that a saturated solution of this nature, if free from solids, may be considerably undercooled without precipitation. The filtrate was evaporated to about 100 cc. in large pyrex beakers, then to dryness in small weighed pyrex beakers. Organic matter was oxidized with strong chromic acid, then the chlorides washed out with dilute hydrochloric acid. Two weighings of the residual silica were made, each after an oven treatment at 160° C. to remove free hydrochloric acid and reduce moisture to 4 per cent. The loss of silica by solution during washing is probably well under 3 mg.

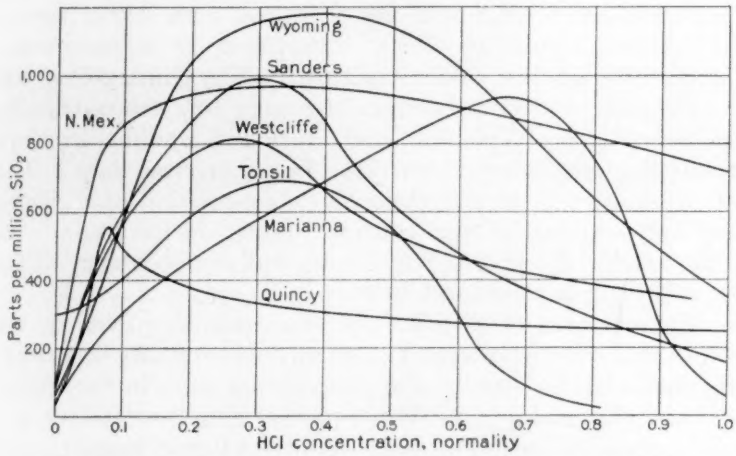
All of the natural clays (1 to 6 in the list) show low solubility (30–50 p.p.m.) in distilled water as would be expected from age-long contact with natural waters and with diffusion of ions in all cases, and percolation in some, continually operating. On the other hand, the prepared bentonite (Tonsil), activated by acid leaching, shows the solubility (300 p.p.m.) of silica gel at 100° C.

The greatest response to very dilute (0.03N—0.1 per cent.) acid is shown by the New Mexico bentonite, No. 5 on the list. This would be expected if it had been exposed only to water relatively free from the organic acids to which the other bentonites may have been exposed. The Sanders bentonite is next in order, followed by the Wyoming.

All seven clays have pronounced maxima of relative silica solubility in the region of 0 to 0.7N HCl. The Quincy fuller's earth has a very sharp maximum of 560 p.p.m. of silica at about 0.08N, Marianna has a broad maximum of 940 p.p.m.

at about 0.7N, the maximum solubility of the remaining five are intermediate between these two values. The highest silica concentration is 1180 p.p.m. shown by the swelling Wyoming bentonite. At higher acid concentrations (not shown) 1.2 and 3.0N, these solubilities all fall toward or below 100 p.p.m., which is the residual concentration of a silica solution not precipitable by an excess of salt.[1, 6] It is of interest to note that the silica of these clays is several times more soluble in dilute acid-salt solutions than is silica gel in water. This greatly increased solubility is not due to the

FIG. 10.



Silica dissolved by dilute acids in p.p.m. Clay and water constant, acid variable.

solvent [1] but to the silica being more loosely held by the clay silicate (plus adsorbed acid) than in silica gel. This point is worth further investigation.

Assuming an exchange of anion accounts for the maxima of silica solubility very simply. With increasing very low acid concentrations, the anions (Cl) are adsorbed more and more on the clay, thus releasing more and more silica. Finally, the osmotic layer becomes so saturated with anions that they begin to attack the cations of the clay (forming soluble salts and new complexes) and the liberation of silica at first in-

[6] T. S. Lovering: *Econ. Geol.*, **18**, 523–540, Sept. 1923.

creases, then decreases, ceases altogether, or is even reversed. Maximum silica solubility thus corresponds with maximum anion adsorption. With the Sanders bentonite the maximum silica solubility occurs at 0.3N concentration of acid and it is at this concentration that iron begins to be removed and the bentonite first shows bleaching power. The free acid remaining in solution is also a maximum at this concentration, as would be expected. With pure silica gel, instead of clay, there is little or no adsorption of anions hence no greatly increased solution of silica.

The *heights* of the maxima of silica solubility are evidently measures of the adsorption capacity (for anions) of each clay. Their *positions* on the acid concentration scale are of course the concentrations at which adsorption is a maximum. Their *widths* are less easily explained. The Quincy clay has an extremely narrow maximum at a very low concentration, the New Mexico, Wyoming, and Marianna maxima are very broad, the remaining three clays being intermediate. The Quincy fuller's earth adsorbs with decomposition only over a very narrow range of acid concentrations, the greater widths of the remaining maxima may be due to inhomogeneity of the clays as regards structural energy.

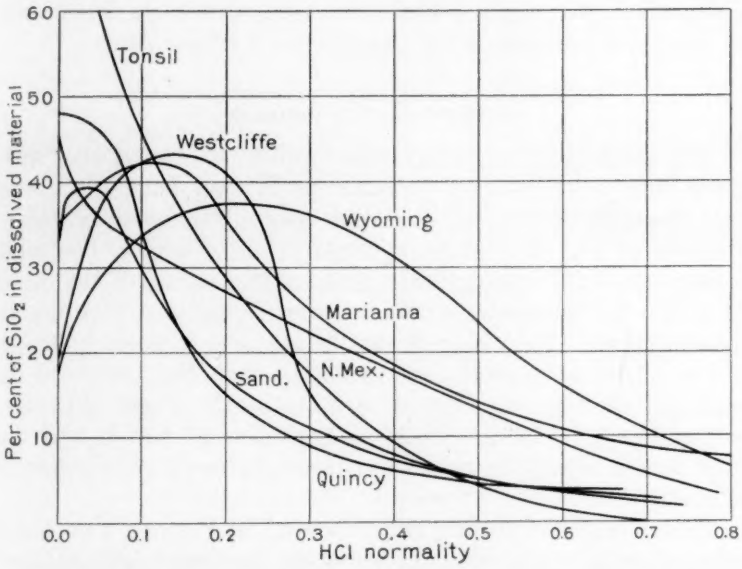
Alumina as well as silica goes into solution, even at the lowest acid concentrations, and dissolves in steadily increasing amounts with increasing acid concentrations. In the higher acid concentrations (1.2—6N), iron and alumina dissolve in a nearly constant ratio and both dissolve in proportion to acid concentration. In very dilute acid the solution of alumina is below normal for Sanders and Westcliffe bentonites and above normal for the remaining five clays. Even the activated bentonite (No. 7) yields some alumina at the lowest (0.03—0.12N) acid concentrations observed. Except for this bentonite in acid concentrations below 0.08N, the alumina dissolved always exceeds the silica, but only slightly near the maxima of per cent. silica. Here the molecular ratio Al_2O_3 : SiO_2 equals 1 : 1 very nearly.

What is the state of the alumina in solution? Is it part of a double alumino-silicate anion, a separate anion or a salt in solution? The solution behaves like an equilibrium mixture of these constituents which is in equilibrium with excess clay

and water. With removal of (1) clay, (2) water and (3) free HCl in that order, of course $AlCl_3$ and SiO_2 remain, but the matter of interest is the solution in equilibrium with clay.

The highly activated Tonsil clay (No. 7) and the naturally active fuller's earth (Quincy, No. 4) yield the highest percentages of silica to pure water, as is to be expected from their bleaching power. Next comes New Mexico (No. 5) whose thermal dehydration curve indicates the presence of consider-

FIG. 11.



Per cent. of silica in dissolved material. The ratio of silica to total dissolved solids is a maximum at very low acid concentrations where *anion* exchange is a maximum. At higher concentrations, *cation* exchange becomes dominant. The activated bentonite (No. 7) has its maximum (94 per cent.) for pure water.

able free or loosely held silica. Marianna (No. 3) ranks high as would be expected from its high bleaching power in the unleached state. Its curve has both the high initial silica of the active clays and the still higher maximum of the raw bentonites. The Sanders clay (No. 1) has a narrow maximum (0.0 to 0.8N acid concentration), and Wyoming (No. 6), which is but slightly activable, has a broad maximum. These characteristics may be a general clue to activability. All the

curves of course approach a low or zero per cent. silica at high acid concentrations.

Other prepared bleach clays (partly acid-leached bentonites) were tested for silica solubility in distilled water. Mississippi Vicksburg yielded silica 504 p.p.m., 96.0 per cent. of dissolved solids, Chito, Arizona, silica 487 p.p.m., 94.6 per cent., an inferior imported bleach clay silica 343 p.p.m., 84.4 per cent. For comparison the solubility of some other materials was tested in 0.2N acid; permutite (Folin), silica 338 p.p.m., 10.7 per cent., brown diabase field soil screened through 150 mesh, silica 362 p.p.m., 16.8 per cent., Colorado River silt (+ 200 mesh) Yuma, silica 145 p.p.m., 5.95 per cent.

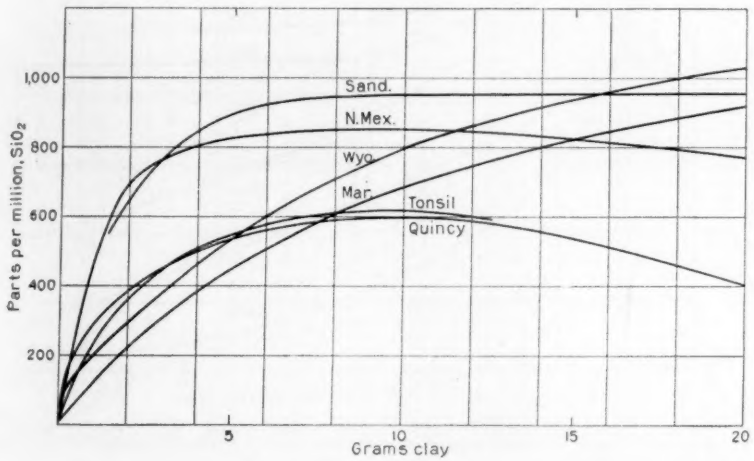
III. SOLUBILITY IN 0.2 NORMAL HYDROCHLORIC ACID. QUANTITY OF CLAY VARIABLE.

The solubilities reported above relate to excess clay and water with acid variable (conditions in clay beds). It was also thought of interest to find solubilities with varying amounts of clay in a given concentration of acid. The acid chosen was 0.2N hydrochloric acid for this is one of the most favorable to the release of silica from the type of clay under investigation. To a liter of this dilute acid in each test was added 0.5, 1, 2, 5, 10 and 20 grams of each clay followed by cooking, filtering and silica determinations. These clay concentrations vary from a cloudy suspension to a mud and the large excess of slightly acid solvent simulates clay suspensions in lakes.

Three types of curves are indicated in Fig. 12, two clays being of each type. The curves of the Sanders (Arizona) and New Mexico bentonites rise quickly and then remain constant at about 900 parts per million up to mud-like suspensions. The two active clays, the fuller's earth, Quincy, and the acid-leached bentonite, Tonsil, rise less rapidly to about 600 parts per million at 10 grams of clay per liter, then fall off. The curves for the Wyoming swelling bentonite (inactive and inactivable) and the Marianna (active and further activable) rise gradually to a high maximum of above 1 gram of silica per liter at above 20 grams per liter in the concentrated suspensions. With but 0.5 gram of these clays (per liter of 0.2N HCl) it was usual to find a large percentage of the clay

in solution after the 24 hour cook. This suggests that conditions exist for clays of this type in which each clay would be completely soluble. The condition for complete solubility is evidently just sufficient acid to take care of the clay bases, combined with sufficient water to dissolve the silica. The filtrate in these tests always contained considerable free acid even when there was a large excess of clay. While other anions are necessary to liberate the silica to dissolve in water, these must be shared between the water and the clay bases. The maximum concentration of silica with respect to clay in

FIG. 12.



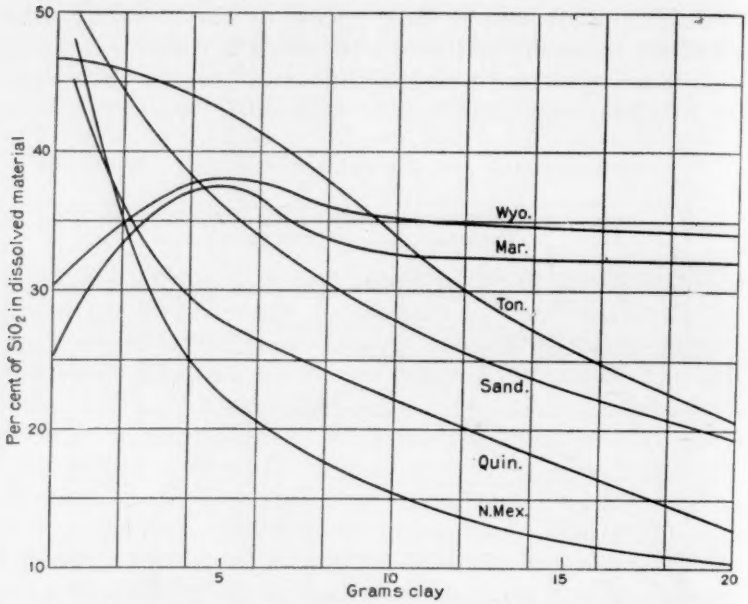
Silica dissolved vs. clay concentration, acid, water and cook constant.

water occurs when this action of the Cl ions is at a maximum. With an excess of clay there may be fewer such ions in solution, owing to adsorption, and less silica is liberated.

The proportion of silica in the material going into solution is roughly equal to that in the clay for small amounts of clay for four of the bentonites, but the Wyoming and Marianna bentonites show much lower proportions, rise to a maximum at 5 grams of clay per liter, the silica then drops slightly to a constant value of about 33 per cent. At 5 grams, clay and acid are approximately equal. As the concentration curves (of silica) for these two clays are rising smoothly at this point

(Fig. 13) the humps on the present curves must mean less chlorides formed. At higher clay concentrations the ratio of silica to chlorides remains constant. With the other four clays, this ratio decreases steadily with increase of clay concentration.

FIG. 13.



Per cent. of silica in dissolved material, quantity of clay variable. The percentage of silica in the material dissolved from six bentonites in relation to the amount of clay digested 24 hours in one liter of 0.2N HCl.

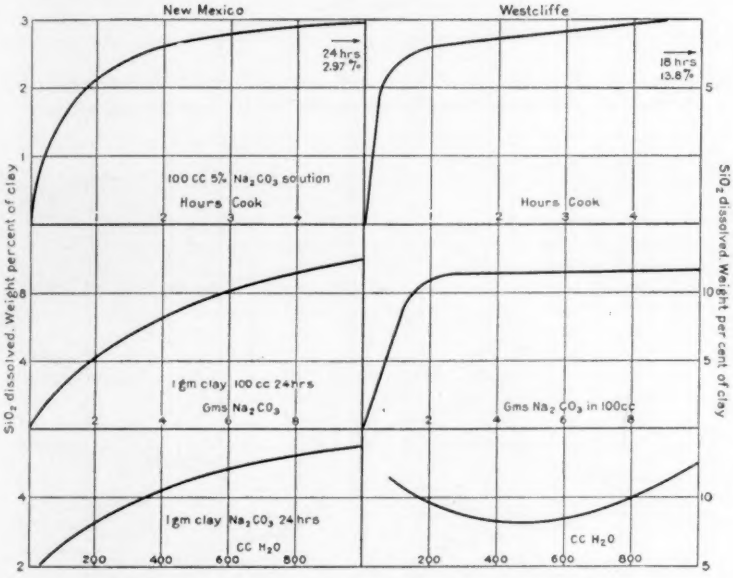
IV. SOLUBILITY IN DILUTE ACIDS AND ALKALIS. WATER VARIABLE.

As dilute alkaline as well as acid waters are common in nature it seemed worth while to investigate their solvent action, particularly in the region of high dilution. This amounts to keeping clay and reagent (acid or alkali) constant and varying the water over a wide range.

The program adopted was to take one gram of clay and one gram of HCl (or Na_2CO_3) in 0.1, 0.2, 0.5, 1.0, 2, 5 and 10 liters of water and determine the silica dissolved as described in Section II. At the higher dilutions all materials were cut down in proportion to make one liter of solvent and the results calculated to the dilution corresponding to one gram of clay.

First, however, the silica dissolved from two bleach clays (Westcliffe and New Mexico) by more concentrated sodium carbonate solutions was determined. The results are summarized in Fig. 14. The upper curves relate to the rate of solution, the middle curves to the results for the more concentrated solutions of sodium carbonate, and the lower curves

FIG. 14.


New Mexico
Westcliffe
24 hrs 2.97 %
18 hrs 13.8 %
100 cc 5% Na2CO3 solution
Hours Cook
1 gm clay 100 cc 24 hrs
Gms Na2CO3
Gms Na2CO3 in 100cc
1 gm clay Na2CO3 24 hrs
CC H2O
SiO2 dissolved. Weight percent of clay
SiO2 dissolved Weight per cent of clay

Westcliffe and New Mexico clays in sodium carbonate solutions.

to some of the more dilute solutions. Results for still more dilute solutions are shown in Fig. 15.

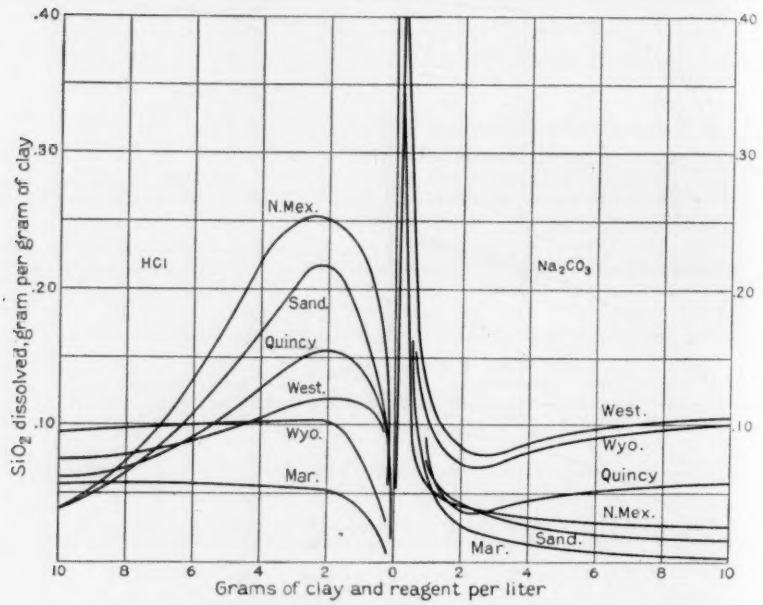
One gram of Westcliffe clay in 100 cc. of 5 per cent. sodium carbonate loses silica rapidly during the first hour but does not reach equilibrium in 5 hours (upper curve). In 3 hours the silica in solution is half that in 18 hours (0.138 gm.). The New Mexico clay, however, approaches equilibrium (3 per cent.) in 4 hours.

Taking one gram of clay in 100 cc. of water, adding 1.0, 2.0, 5 and 10 grams of sodium carbonate and cooking 24 hours at 98° C., the yield of silica in the Westcliffe clay reaches

equilibrium (11 per cent.) in 2 per cent. solution while that of the New Mexico clay is still rising steadily at a concentration of 10 per cent. (middle curves).

The ordinary test for "soluble" silica, namely, cooking 1 gram of clay in 100 cc. of 5 per cent. sodium carbonate solution for 15 minutes and determining the silica in solution, is seen to be of little significance for such clays as these since the

FIG. 15.



Solubilities of clay in dilute acid and alkali solutions.

results may be far from equilibrium as regards either time or concentration.

Also shown in Fig. 14 (lower curves) are the results for variable amounts of water using 1 gram of clay and 1 gram of sodium carbonate in 200, 400 and 1000 cc. of water and cooking 24 hours at 98° C. Both clays show increasing silica solubility with increasing quantity of water but the Westcliffe has a pronounced minimum near 400 cc. of water while the New Mexico clay rises steadily.

Similar experiments with 1 gram clay : 1 gram hydrochloric acid shows a similar increase of silica solubility with increasing quantity of water at first followed by a gradual fall in solubility with increasing dilution. The tests were next carried progressively to a dilution of 10 liters for both hydrochloric acid and sodium carbonate.

The percentages of silica dissolved at different dilutions of both acid and alkali are shown in Fig. 15 and in Table 3.

TABLE 3.

Silica (Per cent. of Clay) Dissolved from 1 Gram of Clay in V Liters of Solution Containing 1 Gram of Hydrochloric Acid or 1 Gram of Sodium Carbonate.

	V	Wyo.	N. Mex.	West.	Sand.	Quincy	Mar.	Pum.
HCl	0.1	9.5	4.0	7.5	4.0	6.2	5.7	2.3
	0.2	10.0	17.5	9.4	13.7	10.6	5.5	2.5
	0.5	10.2	25.2	11.8	21.8	15.5	5.2	2.5
	1.0	7.0	22.6	11.5	16.4	14.3	3.8	2.0
	2.0	4.5	18.5	10.7	12.4	12.0	2.3	—
	5.0	2.2	13.0	8.5	7.3	8.0	0.7	—
	10.0	0.4	0.9	0.8	0.7	0.6	0.1	—
Water	∞	0.17	1.1	2.0	1.2	2.0	0.0	—
Na_2CO_3	10.0	16.9	34.3	51.0	4.0	3.2	6.9	—
	5.0	48.1	33.6	27.5	41.5	25.3	45.2	—
	2.0	21.5	10.6	17.5	11.0	19.2	16.0	—
	1.0	10.4	5.4	12.5	7.2	7.9	6.2	7.0
	0.5	7.0	4.2	8.3	4.2	3.7	2.3	4.7
	0.2	8.6	3.1	9.4	2.4	5.0	1.0	2.5
	0.1	10.0	2.6	10.5	1.7	5.9	0.3	1.5

Results for pumice, similar to bentonite in composition, have been added in Table 3 for comparison. Its solubility in alkali is very similar to that of the Sanders bentonite, and in acid is lower than that of any bentonite.

The curves for the New Mexico clay in acid indicate that 4 grams of hydrochloric acid in 1200 cc. of water would completely dissolve 1 gram of this clay. A special test showed at least 95 per cent. in solution. This solution (water-white and showing no Tyndall beam) was filtered and slowly evaporated in an attempt to obtain montmorillonite. Free acid was kept down by placing an alundum crucible containing silver carbonate in the solution. The resulting product under the microscope resembled montmorillonite.

As these tests were run in pyrex flasks and beakers, blanks (clay omitted) were run to determine the silica dissolved from the glass. The blanks with acid (1.0, 0.5, and 0.2 grams per liter) yielded but a fraction of a milligram per liter. The blanks with sodium carbonate (after acid) showed silica dissolved to the extent of only 1.5 per cent. of the alkali. Duplicates and checks by different methods showed satisfactory two figure accuracy. A test with sodium chloride 0.2 gm./liter, on equal amounts of Wyoming, Quincy and Sanders clay gave solubilities considerably less than for pure water. The addition of ammonium chloride to hydrochloric acid (2 grams of each and 2 grams of clay to one liter of water) did not affect the solubility. Nitric, sulphuric and phosphoric acids all release about the same amount of silica from Sanders clay as hydrochloric acid with maxima at nearly the same concentration. Oxalic acid gives a much higher maximum (31.2 per cent.) also at 2 grams per liter. Acetic, tanic and humic acids release only about 2 per cent. silica, between 2 and 4 grams per liter.

There are pronounced maxima of solubility for both the acid and alkaline solutions. On the acid side the maxima occur near 0.5 liter of water per gram of hydrochloric acid per gram of clay. On the alkali side they occur at much higher dilutions. The maximum silica dissolved by very dilute alkali is nearly all that contained in the clay, the lowest maximum is about half (for the Quincy fuller's earth).

THERMAL DEHYDRATION.

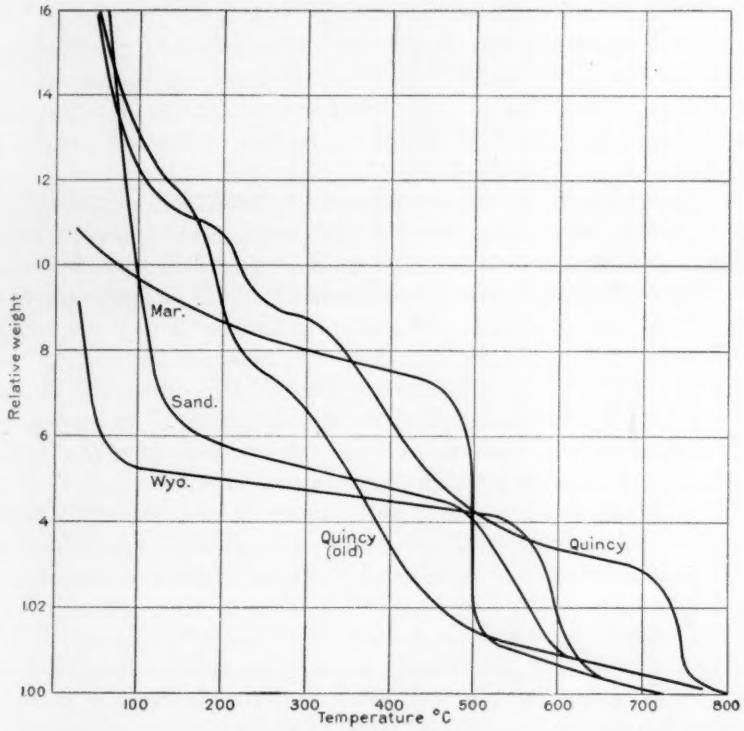
Typical thermal dehydration curves for bentonite are reproduced in Fig. 16, Sanders and Wyoming. Nearly all bentonite curves lie between or near these two curves. The large drop below 100°, the uniform slope 200–500° and the shoulder between 500 and 650 are characteristic. These bentonites, after acid leaching to bleach clays, give the same thermal dehydration curves,[7] but slightly lower; the shoulder near 600° remains but is lowered. There are indications of a hydrate ($8H_2O$?) stable at low temperatures and in excess water. When the logarithm of the water in the clay is

[7] "The Bleaching Clays," Circular 3, U. S. Geological Survey, 1933.

plotted against 1/T these thermal curves break up into three straight lines indicating three definite energies of hydration.

The fuller's earth (Quincy) exhibits two extra shoulders (hydrates?) at about 200° and 300°. These two hydrates appear to be more stable than the one at higher temperatures, the latter completely disappeared in a sample room-dried for

FIG. 16.



Thermal dehydration.

four years. One bentonite having a pronounced shoulder at 200° when fresh, lost it without trace after a month room-dry. Another lost about a fifth of the 500° shoulder after three months' drying, touching the original curve only at 160°. The Marianna curve is that of a beidellite rather than a bentonite. Much remains to be done in tracing out the alteration of bentonite to fuller's earth.

SUMMARY.

Of the five varieties of bleach clays distinguished by acid leach and oil bleach tests, namely, the

Inactive and almost inactivable bentonite (e.g. Wyoming)
Inactive but highly activable (Sanders, Westcliffe)
Naturally active fuller's earth (Quincy)
Artificially activated (Filtrol, Tonsil)
Active and further highly activable (Marianna)

all show the same lattice (X ray) structure and no essential differences in refractive indices, thermal dehydration, or chemical composition. All are dominantly the clay mineral montmorillonite. The bleaching action is thought to be a surface effect on minute molecular groups.

The highest bleaching power (adsorption capacity) is attained by the rapid removal with moderately strong acid of about two-thirds of the bases of an activable bentonite.

Activable bentonites are converted to fuller's earth by slow leaching in dilute acid (1 per cent. or less) at low or moderate temperature and are not further activable.

The solubilities of these five varieties of clay in acid and weak alkali solutions fail to reveal differences characteristic of their bleaching power. However, the silica of active clays is apparently more soluble than that of inactive clays.

All of these clays show pronounced maxima of silica solubility at low acid and at still lower alkali concentrations. These maxima are far higher than the solubility of fresh silica gel in water.

Applications of these results to the activation of bleach clays, to the soil problem of plant food and to the chemical problem of the solubility of silica and the deposition of silica from solution are indicated.

LIMITATIONS OF HIGH VOLTAGE INSULATION.

BY

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Not many years ago a distinguished electrical engineer expressed the opinion that electrical transmission distances would never go much beyond 150 miles, and transmission voltage would not rise much above 110,000 volts. He stated, as grounds for this opinion, that throughout this country the distance between available sources of power, either hydraulic or steam, was nowhere greater than about 300 miles. Notwithstanding this authoritative opinion, we now have a number of installations that show that the estimate of the future limit of the distance of transmission was better than that as to the figure of transmission voltage. We have comparatively few transmission projects for distances greater than 150 miles, but there are a number of such projects in which the voltage is 220,000 volts. A conspicuous example, in which both estimates have been exceeded, is the Boulder Dam-Los Angeles transmission, over a distance of 300 miles, and at a voltage of 287,000 volts. In this as well as in many other cases, special considerations other than that of the nearest power supply have indicated an economic advisability of power development and transmission to greater distance and necessarily at higher voltage. In view of these rapid advances in the figure of standard transmission voltages, within a comparatively short period, it is of interest to ask what engineering limitations or restrictions will be likely to arise in case still greater distances and higher voltages are proposed. It is our purpose here to examine briefly the limitations likely to be placed on a further increase of transmission voltage by the insulating properties of present available materials.

The Insulating Materials: The materials most commonly used for the insulation of high voltage power circuits are the atmospheric air, ceramic materials such as glass and porcelain, refined petroleum oils, and various composite saturated

fibrous materials such as impregnated paper. All these materials, when carefully purified and protected have high insulating properties. Their inherent or initial values if maintained, would be sufficient for meeting for sometime the demands of our steadily mounting values of transmission voltage and power. Unfortunately, however, these initial values cannot be maintained in high voltage service. They suffer serious lowering owing to unavoidable modifications during the normal processes of manufacture, transportation, installation, and operation. Thus the very conditions of manufacture and service impose important limitations on the degree or extent to which the inherent properties of insulating materials may be utilized.

The important electrical characteristics of the materials used for the insulation of high voltage circuits are conductivity and dielectric strength. Dielectric strength is the ability to withstand breakdown or actual failure and short circuit, and is the first essential of safe insulation. The conductivity is a measure of the ability of the material to withstand slow leakage. It must be kept within certain low limits in order to prevent constant energy loss which, in turn, causes internal heating and ultimate lowering of dielectric strength. Specific inductive capacitance is relatively unimportant in the insulating function of dielectrics.

All materials, including the liquids and gases, have some electrical conductivity. The conductivity of known materials varies over a very wide range. For example, that of a good mineral oil is 10^{-15} mhos, and that of copper 10^{5} mhos per cu. cm., a ratio of $1 : 10^{20}$. However, most materials fall into two widely separated groups with values of conductivity well out towards the extremes represented by the foregoing figures. Thus we have a broad division of known materials into *non-conductors* or insulators, and *conductors* in which the conductivity is very high. The conductors are conspicuously represented by the metals and need not concern us here. Materials of high insulating value are found amongst gases, liquids, and solids, all commonly known as dielectrics. Several conspicuous examples have been mentioned above, but even within this group of insulating materials, low conductivity is a relative term and may vary as much as a million times between

two materials, say between 10^{-12} and 10^{-18} mhos, both of which might still be classified as available for high voltage insulation.

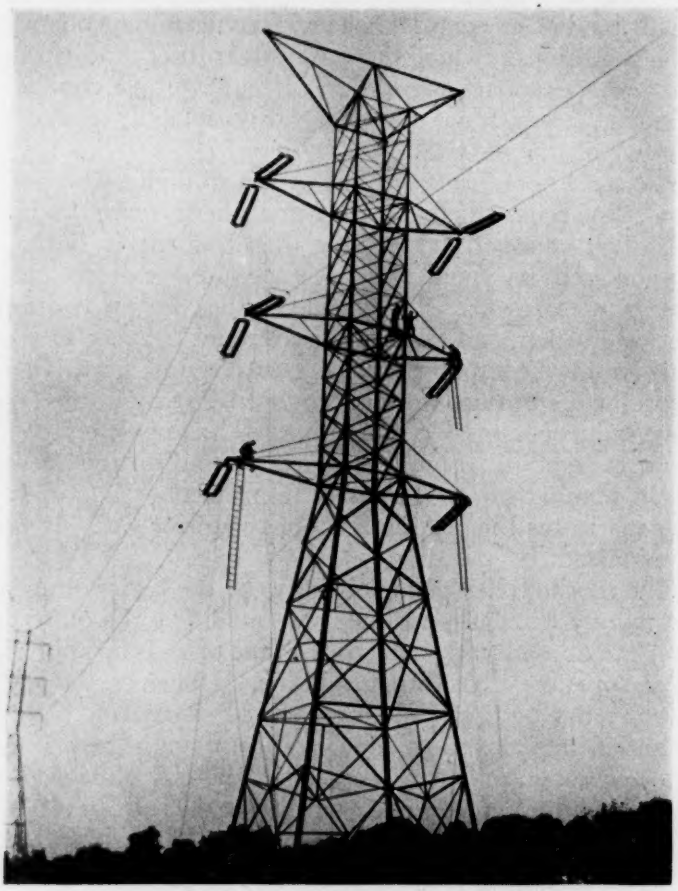
All materials used for high voltage insulation must necessarily have high dielectric strength. It is not possible to state specifically the dielectric strength of particular materials because behavior, as regards dielectric strength, depends widely on the conditions in which the materials are used, and especially on the shape and configuration of high voltage conductors. Dielectric strength is not necessarily related to the conductivity of the material.

The Air as an Insulator: The overhead high voltage transmission line relies chiefly on the atmospheric air for its insulation. The conductivity of dry dust-free air is quite low. This conductivity is due to an average number of free gaseous ions always present. The gas molecules are in continuous kinetic agitation, and some of the collisions between molecules result in the separation of the positive and negative ions. Molecular disruptions are also caused by stray x-rays, radioactive influence, or by cosmic rays. The oppositely charged ions soon combine or find new partners, but on the average a certain number of free ions will be present at all times and this constitutes the conductivity of the air or gas. It is said to be ionized.

The conductivity of the air between the high voltage conductors of a transmission line is so small as to be quite negligible, and at moderate values of voltage there is no appreciable leakage or energy loss through the air. However, the few ions present move back and forth under the alternating high voltage and if they move fast enough, they may, in their collisions with neutral ions, create new ions, thereby causing an increased conductivity. The velocity of the ions depends primarily on the electric field intensity or voltage gradient. The field intensity is greater near the conductors than in the central region between them, owing to their circular shape and small diameter. Consequently, the air near the conductor is subject to the highest stress and as the voltage is increased, the air at the surface of the conductor breaks down first. This is seen in the well known *corona* or brush discharge surrounding the conductor. Corona formation, however, is not necessarily

followed by complete breakdown and short circuit. This is due to the fact that the voltage gradient at the surface of a round high voltage conductor is lower, the greater the radius

FIG. 1.

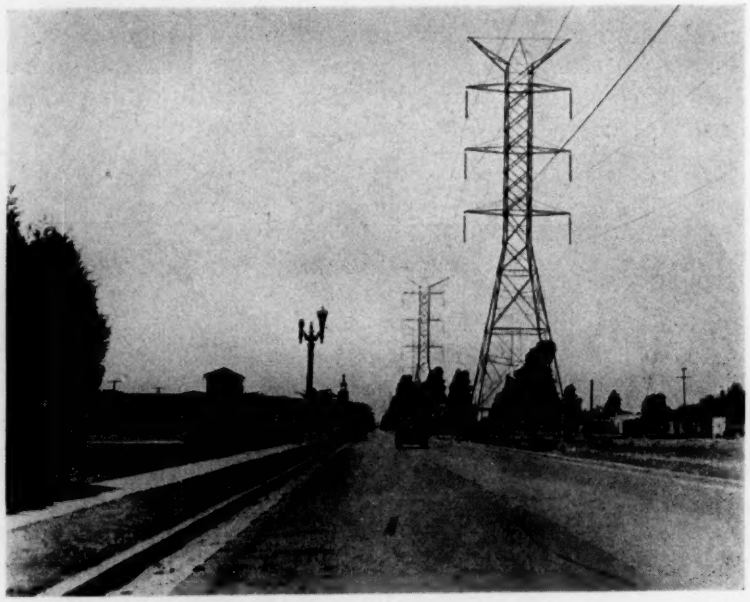


Boulder Dam transmission line, city of Los Angeles.
Showing normal type of Double Circuit Strain Tower with opportunity to judge scale from workmen, automobiles, etc.

of the conductor. Consequently when corona forms, being highly conducting, it increases the effective radius of the conductor to a value for which the surface gradient is equal to, but

not greater than the electric strength of air. Still higher voltage and larger corona are required for complete breakdown and spark-over. The dielectric strength of air between parallel plates is about 30 kv. per cm.; as measured by the appearance of corona on a round wire, it increases with decreasing radius of curvature of the wire and thus becomes higher as the diameter of the transmission conductor is reduced.

FIG. 2.



Boulder Dam transmission line, city of Los Angeles.

For small wires a gradient of 90 kv. per cm. or higher at the surface may be reached before corona forms.

Corona causes increased conductivity and energy loss, attacks dielectric materials, and is thus a limitation to the insulating properties of the air. Up to the present, even with recent large increases in voltage values, it has been possible to prevent corona by suitable and careful design of the transmission line. The measures to be taken are increased separation between conductors and increased diameter of the conductors,

since both these measures raise the corona forming voltage. The extremes to which they have been pushed by the ever-increasing tendency to higher transmission voltages are exemplified in the 287 kv. lines between Boulder Dam and Los Angeles. In these lines the space separation of conductors is about 24 ft. The diameter .814 in. of the necessary stranded conductor for the power current, has been increased to 1.4 in. without increasing the amount of metal, by means of a highly ingenious type of hollow line conductor. This is the well known Type HH conductor which is made up of interlocked spiralled strips formed into a hollow cylindrical cable which nevertheless has high tensile strength, flexibility, and other mechanical properties necessary in transmission line construction. This conductor also has an over-all smooth

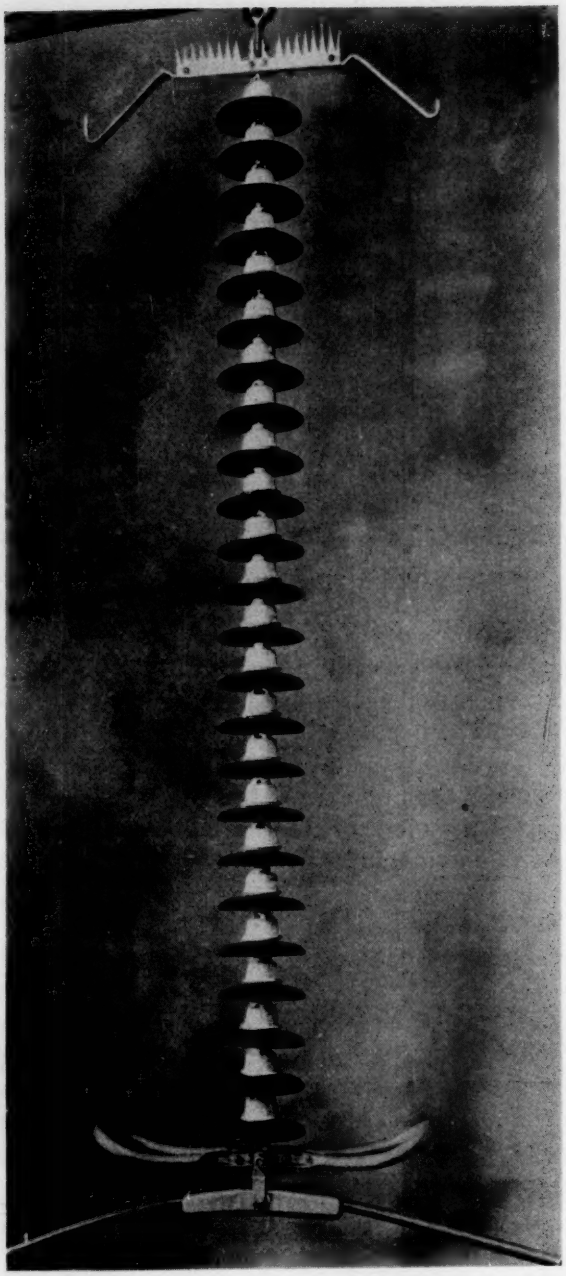
FIG. 3.

Hollow conductor for Boulder Dam-Los Angeles 287-kv. transmission line. Diameter 1.4".

surface which still further raises the corona forming voltage above that of the usual stranded cable of the same diameter. The corona forming voltage of the Boulder HH conductor, when smooth and clean would be about 450 kv.; the line voltage is about 285 kv. Actually, when erected and due to processes of handling, erection and weathering, a small corona loss appears at 240 kv. However the loss is still small at operating voltage; it is only 60 per cent that of a stranded conductor of the same diameter, and this difference becomes increasingly great at higher voltages.

Thus so far as the open air is concerned, the limitations of its insulating properties are already imposing exceptionally wide spacing, higher towers, and special types of conductor in the increasing tendency to higher voltages. Still further increases in voltage will require even more elaborate and costly

FIG. 4.



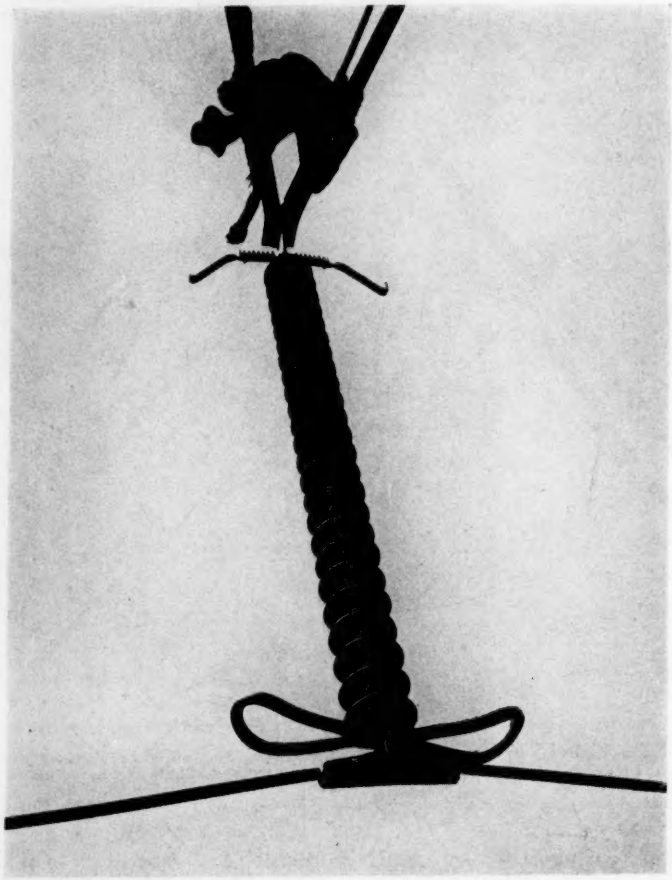
Suspension insulator assembly. Boulder Dam Transmission line, city of Los Angeles.
Consisting of 24-10" diameter, 5" spaced porcelain insulators, upper arcing horn of 1½" × ⅜" steel strap with bird guard, lower arcing horn of 1¼" standard iron pipe, and "Free Center" anti-fatigue type of suspension clamp of special design to avoid corona and provide support for conductor by means of two trunion mounted saddles.
Vertical distance between arcing horn tips, 110½".

methods of line construction. These will increase correspondingly the capital costs. Thus the limitation imposed by the air as an insulator in long distance transmission appears in the form of a very decided economic limit in further increase in transmission voltages.

The Porcelain String Insulator: The high power transmission conductor must be supported well above the surface of the ground, and it is obvious that the support itself must possess high insulating properties, combined with high mechanical strength and flexibility under all weather conditions. Again using the Boulder Dam lines as an extreme example, the weight of this line and its insulators in a normal span of 1,000 ft. is about 2,300 lbs. per conductor. In storms of sleet and wind, the weight on the supports may be increased several times. The only insulating materials which will stand up continuously to the extreme weather stresses in open lines are the porcelains and glasses assembled in strings of individual units. Intensive study and development have resulted in remarkable improvements in both the electrical and the mechanical properties of these ceramic materials and in the methods for their incorporation into the metallic elements of the modern suspension type of insulator. Recent studies of the internal stresses in the surface of the porcelain insulator, and of their control through that of the material for the surface glaze, have increased the toughness and anti-breaking properties by 15 per cent. The breaking strength of the modern porcelain insulator under tension reaches the neighborhood of 15,000 lbs. and the flexibility and other mechanical properties of the modern insulator string are admirably adapted to the demands upon it. Good ceramics have negligible leakage and loss, and electric failure is not apt to occur except as the result of cracks or other imperfections. These are not apt to rise in service except after long periods of extremes of temperature and moisture. Dust and other deposits on the surface may result in leakage or brush discharge, in which case there is increased tendency to surface cracking. In general, however, it may be said that so far as the porcelain itself is concerned, it does not constitute one of the major limitations of high voltage transmission.

Nevertheless strong though it is mechanically and electrically, the insulator string is commonly the weakest point of the line. Not inherently, for by increasing its length it may be designed without difficulty for reliable operation under

FIG. 5.

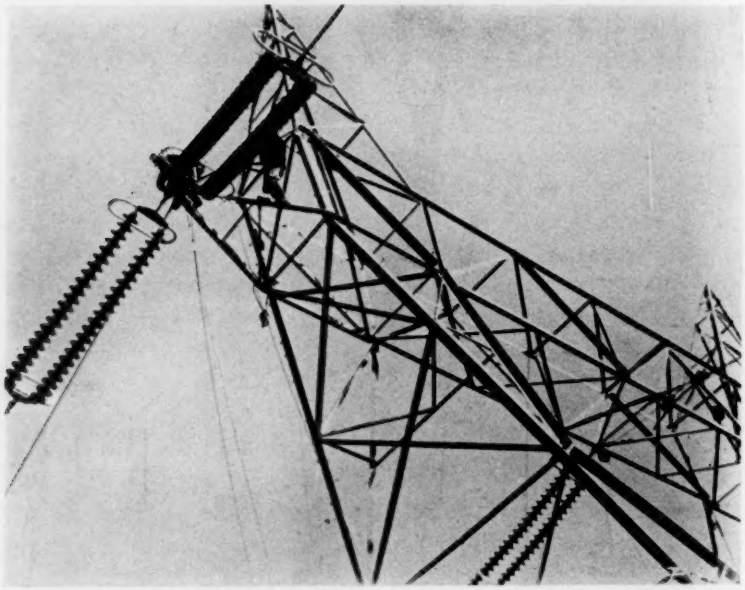


Suspension insulator assembly on tower. Boulder Dam transmission line, city of Los Angeles.

any normal value of line voltage. Its weakness arises in its vulnerability in moderate lengths to the excessively high transient voltages which occur on the line during thunder storms. When, as often happens, lightning actually strikes

the line, it receives within an extremely brief interval, a high value of electrostatic charge which induces a correspondingly high value of voltage to ground. The charge must "spill over" to earth somewhere, and the insulator string is usually the preferred path. The 60 cycle dry flash-over of a single insulator unit is about 100 kv. A much lower average figure must be employed in fixing the number of units in a string,

FIG. 6.



Pulling strain insulator string into final position on single circuit tower, Boulder Dam transmission line, city of Los Angeles.

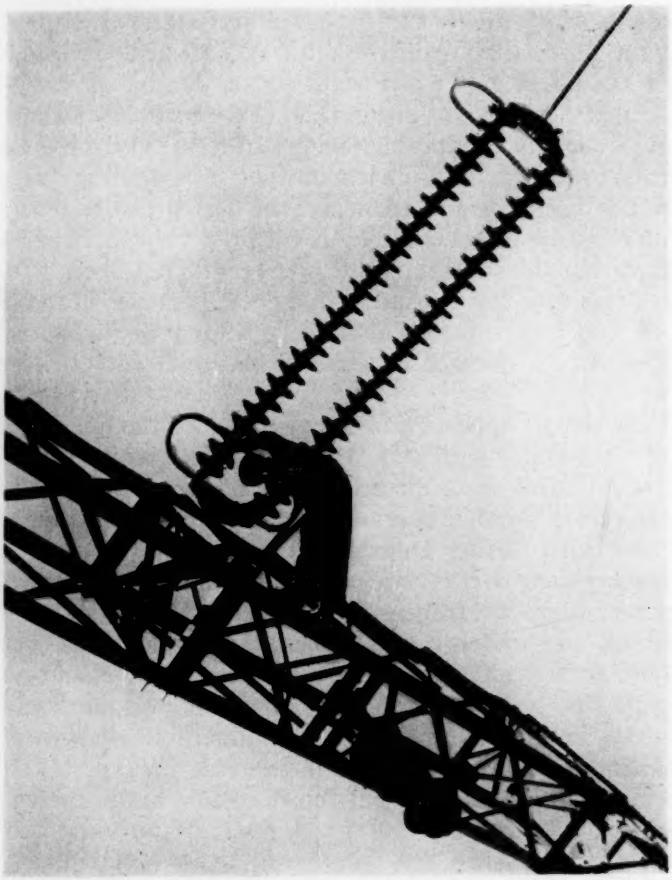
Such strings consist of double strings of 22-10½" diameter, 6" spaced porcelain insulators, upper and lower yokes carrying 1¼" standard iron pipe arcing horns on their upper side, dead end clamp and attachment clevis fittings.

Distance between arcing horn tips, 118¾".

owing to weathering, and non-uniform voltage gradients. The number of units must be still further increased in order to reduce flash-over from lightning strokes. The insulator strings of the Boulder lines contain 24 units; at 166 kv. to neutral this is only 8.3 kv. average stress per unit. The Boulder string is 10 ft. long. For complete insulation of the abnormal voltages caused by lightning, the number of units

in series and the length of string become prohibitive. Occasional lightning flash-over is accepted as a necessary evil with some compensation in its safety valve action. Thus the insu-

FIG. 7.



Strain insulator string at terminal station rack. Boulder Dam transmission line, city of Los Angeles.

Such strings and similar strings in use on double circuit towers (light loading district). Consist of double strings of 26-10″ diameter, 5″ spaced porcelain insulators, together with same hardware as used throughout the line.

Distance between arcing horn tips, 116¾″.

lator string has so far kept up with increases in line voltage, but is far from meeting the voltages caused on the line by lightning.

The lightning flash-over of an insulator is in itself not as objectionable as is the power arc that follows it. The heat of the arc is highly dangerous to the porcelain and often destroys the insulator. As a protective measure the ends of the insulator string are often equipped with metallic arcing rings, horns, or screens which divert the discharge and arc to air gaps away from the porcelain. Another more recent measure is the so-called expulsion gap which consists of a tube of insulating material attached to the ground end of the insulator string, and having a slightly conducting inside surface. The other end of the tube forms an air gap with another tube or an arcing ring. When the discharge and arc occur, the high pressure generated within the tube blows the arc out within a very short period of time, so that the station circuit breakers do not open. Measures of this type have resulted in a great decrease in the number of line interruptions due to lightning disturbance and consequently a notable increase in the reliability of electric power supply.

Thus the air appears as a safety valve for the line insulator string, and under such conditions the latter so far stands up very well. But it is already too long, and the provisions necessary for reliable operation must increase in complexity and cost with further increases in voltage.

Underground High Voltage Cables: High voltage overhead lines terminate in transformers, circuit breakers, lightning arresters, and underground cables. The first three types of equipment are all stationary, of water-proof construction, and suffer no serious limitations as to insulation under normal operating conditions. Their most vulnerable element is the insulating oil in transformers and circuit breakers. This is extremely subject to chemical deterioration, but in these types of apparatus it can be carefully protected, and inspected and renewed as necessary.

The high voltage underground cable, however, presents quite a different picture. Its insulation is subject to many limitations and it presents many interesting problems to the research engineer. In its present development it constitutes a remarkable tribute to the knowledge, skill, and enterprise of those participating in that development. Such cables are largely used for the underground transmission and distribution

of alternating electric power in large communities. The range of voltage for this service is from 15 to say 66 kv. In recent years the extraordinary increases in the amounts of power to be transmitted and exchanged through station inter-connection, with consequent crowding of underground duct space, has led to the development of extra high voltage cables, of which there are now in operation a number of installations at 132 kv. and a few up to 220 kv. This sharp increase of voltage within a short period has been accomplished by careful study and research as to the limiting properties of the constituent materials, and by constant and increasing care in manufacture and handling in order to conserve them.

Let us review some of the conditions and difficulties to be met in the successful operation of the high voltage underground cable. The cable is laid or drawn into a duct 4 in. or 5 in. in diameter. Within this space we find a central conductor from ½ to 1 in. in diameter, surrounded by a wall of insulation from ½ in. to 1 in. thick. This, in its turn, is surrounded by a closely fitting lead sheath for preventing the admission of air and moisture and perhaps an outer armor for mechanical protection. Some idea of the high insulating properties necessary for such a thin wall of insulation may be had in noting that the space separation of overhead lines operating at the same voltage would be from 15 to 20 ft. The maximum stress on cable insulation in certain cases is as high as 300 volts per mil.

Impregnated Paper: The insulation of such cables is usually composed of paper impregnated with oil. The paper ribbon about 1 in. wide and .005 in. or more thick is wound on the central conductor in spiral fashion, the joints between ribbons being staggered in successive layers. After elaborate vacuum and heating treatment for the elimination of moisture from the paper, oil equally carefully treated, is admitted and by capillary action is rapidly and thoroughly adsorbed into the paper. The whole is then covered with lead by an extrusion process. In extra high voltage cables, the lead may be applied before impregnation.

These materials and types of construction are largely necessitated by the unavoidable conditions arising in the processes of manufacture, transportation, installation, and

ultimate service. Manufactured in lengths of 500 ft. or more, the cables must be coiled on reels of such size that they may be shipped on freight cars, thus imposing a bending of the cable into a relatively short radius, with corresponding tension and compression on the insulation. This is met, in oil impregnated paper by the slipping of the paper tapes over each other, and a tendency to return to place as the cable is straightened. These processes are intensified in installation by unreeling and reverse bending, when feeding the cable into a manhole and duct. All these operations impose similar strains on the lead sheath which must remain perfectly intact against the smallest opening through which moisture might penetrate, or oil escape.

After the cable is installed, it is stationary and here it would appear that we might reasonably rely on the inherent properties of the insulating materials. Unfortunately, however, the materials which we have assembled as about the only ones which can safely meet the conditions imposed by manufacture, transportation, and installation, do not pull together very well even in normal operation. Cables carry current, and the cable is heated thereby. Conductor, insulation, and lead sheath all expand under temperature elevation. The coefficient of thermal expansion of impregnated paper is much greater than that of lead. Consequently on heating, the lead sheath is stretched, and being inelastic, on cooling does not return to its former diameter. As a consequence gas spaces appear within the wall of the insulation. These gas spaces, particularly at low pressures, break down easily into glow discharge under electric stress and cause the familiar internal gaseous ionization of cables. As alternate expansion and contraction goes on day after day with the normal variations of loads, the condition becomes further aggravated with time. The glow discharges are very active chemically, attacking the paper and oil, thereby increasing the internal conductivity and losses. This causes a progressive reduction of carrying capacity and ultimately leads to failure.

Many devices, methods, and modification of design have been utilized for combatting gaseous ionization. Obviously the simplest is to restrict the temperature variation by a limitation of the amount of current carried, and also to limit the

internal voltage gradient by increasing the thickness of the insulation. Such measures lead, however, to increased sizes and costs or to limited load ratings. They are in fact the dominating limitations in the so-called "solid" cables impregnated with viscous compound, for operation in the range of moderate voltages.

More interesting and very effective are the measures used in cables for very high voltages, say 100 to 220 kv. These are found in the so-called "oil-filled" and the various "pressure" systems. The oil-filled cable is impregnated with a very thin oil and channels are provided through the centers of the conductors or elsewhere, whereby the oil can flow freely at all times to all parts of the insulation. As the latter expands and contracts, the oil may flow out of or into the insulation as needed, the feeding channels being connected to protected oil reservoirs under suitable pressure. In this way stretching of the lead sheath is minimized and there is greatly reduced tendency to the formation of gas voids. In the several "pressure" systems the cable is installed in a somewhat larger metal pipe, completely continuous and closed, and which is subjected to high pressure, say up to 200 lbs. per sq. in. The principle here is that breakdown strength is increased by pressure and that thermal expansion and ionization are restricted; on cooling both lead sheath and internal insulation are compressed into approximately their original condition. In one system the pressure is applied to the leaded cable by means of gas in the pipe casing. In another system the pressure medium is oil and the lead sheath is omitted from the cable. The pressure systems obviously require special ducts and more or less elaborate auxiliary apparatus in the way of reservoirs, pressure operation, control, and recording. Oil-filled and pressure cables are, therefore, employed only in installations of major magnitude. Familiar examples are the 132 kv. oil-filled installations in Chicago and in New York, and the pressure cables through the Baltimore tunnels of the Pennsylvania Railroad electrifications.

The satisfactory performance of these extra high voltage cable systems, particularly that of the oil-filled installations, over a period of seven years or more constitutes an impressive example of the advances possible through scientific research

and resourceful experimental development. Not only have voltage ratings been carried steadily upward to the figures already mentioned, but the voltage gradients of such cables are higher by three or four times than those in the best available insulation of ten years ago. Moreover, internal gaseous ionization, as indicated by a continuous program of suitable measurements, has been greatly reduced if not entirely controlled. Note, however, that the cable is no longer self-contained. The inherent limitations in materials and assembly begin to appear, and the high voltages have necessitated costly auxiliaries.

Instability in Impregnated Paper: Notwithstanding the somewhat glowing picture presented in the foregoing paragraph, we still have before us in the underground cable a most serious limitation, namely the instability or tendency of its insulation to deteriorate. The inherent properties of impregnated paper, when carefully prepared and in its original condition are perhaps superior to those of any other known type of insulation, certainly for adaptation to this purpose. Its conductivity may be reduced to the lowest known range say from 10^{-16} to 10^{-18} mhos. Its dielectric strength over long periods may be higher than 1000 volts per mil. While these extreme values may only be reached under carefully controlled laboratory conditions, nevertheless even in ordinary processes of manufacture, with sufficient care the original properties of the completed cable may be carried to high figures. In sustained service, however, there is always a more or less gradual process of change in the direction of deterioration. The causes of this are not completely understood. The inherent electrical conductivity of carefully purified oil (of the order of 10^{-16} mhos) is so low as to indicate an extremely limited volume of original free ionic content. However, the least impurity, particularly if susceptible to chemical dissociation, will greatly increase the inherent conductivity. Such impurities difficult to completely exclude in manufacture, are traces of moisture, of air, and of electrolytic solids in either oil or paper. The most careful manufacturers wash the paper pulp with distilled or purified water for the elimination of traces of electrolytic content. Under the lowest vacua moisture and air will cling by adsorption to paper fibre. Their

degrees of activity as dissociation and ionizing agents are still unknown and are at present the objects of intensive experimental study. In continued service gaseous ionization tends to increase slowly and to liberate further gas from the oil. Conductivity and dielectric loss also increase due to these exceedingly elusive causes, their continued action being in some way progressively intensified by the combined influence of chemical change activated under temperature elevation and high electric stress. The nature, causes, and elimination of these changes constitutes the most important problem of the cable engineer. At present intensive study is being directed to the influence of traces of oxygen as a direct deteriorating agent, and as related to the catalytic properties of copper and lead. Great progress has already been made, increased precautions and protection in manufacture have already accomplished much. High grade cables may operate satisfactorily for twenty years or more, and the country-wide records of cable troubles and failures have been reduced to remarkably low figures within recent years. As long, however, as these progressive changes, however slow they may be, are known to be present, the cable engineer finds a serious limitation to higher values of voltage.

Summary: It is no new thought that the saving in conductor material at higher transmission voltages is partly offset by the increased cost of insulation. Obviously the higher the voltage the greater the cost of insulation, and the minimum total cost must always determine the most economical value of voltage. In the early days of ascending voltage it was only a question of how much additional insulation was necessary, and the cost of added material. Now however we have reached a stage in high voltage values where the inherent insulating properties of materials are often surpassed in simple forms of assembly, and where physical dimensions are becoming prohibitively great. In order to meet these limitations special forms of construction of the conductor system, and special auxiliaries to the insulating system have become necessary, thereby causing not only greater increases in the cost of insulation, but also clearly marked physical limitations to further elevations of transmission voltage.

High Capacity Attained by New Sulphur Melter.—J. W. SCHWAB AND W. W. DUECKER. (*Chemical and Metallurgical Engineering*, Vol. 44, No. 8.) In very few chemical processes is sulphur used in a solid form. The procedure of melting before use is generally accepted as standard practice. It is simply removed from the stock pile, dumped into rectangular tanks fitted with steam coils and allowed to remain there until fluid or until ready for use. Sulphur, however, is a poor conductor of heat and because of inadequate equipment the melting operation is sometimes slow and bothersome. The Texas Gulf Sulphur Co., as a result of experimentation, has developed improved equipment for doing this. The new melter, designated the Tegul sulphur melter consists of a rectangular tank or shell provided with steam coils at its sides and in its interior. The lower part of the shell is provided with inclined steam-jacketed, V-shaped troughs, the crests of which are about 10 inches apart. Slightly above these troughs and directly over their centers are placed additional steam coils. To these inclined troughs and to the steam coils directly over their centers may be attributed the novelty and efficiency of the new apparatus. The operation of the melter is simple. Sulphur is charged into a hopper over the melter and its weight presses it against the steam coils and heated troughs. The steam coils directly over the troughs prevent bridging and insure a constant feed of sulphur to the heating surfaces. The melted sulphur flows in the inclined V-shaped troughs and is discharged as fast as it is formed through a series of small openings in the side of the shell into a steam jacketed trough on the outside of the tank. From this point it may be conducted to a sump or place of use.

R. H. O.

NOTES FROM THE BARTOL RESEARCH FOUNDATION.

A NUMERICALLY CONSISTENT CORPUSCULAR THEORY OF COSMIC RAYS.*

BY

W. F. G. SWANN.

Theories for consideration divide themselves into two categories, those in which the primaries function as the measured entities, and those in which secondaries or higher order radiations play a significant or even a dominant rôle.

Primaries as Measured Entities. There exists a curve relating altitude and latitude, such that the rays which can just penetrate the earth's magnetic field at an assigned latitude can penetrate the atmosphere down to the altitude given by the curve. The curve cuts the sea-level axis at a latitude customarily associated with that at which the increase of intensity with latitude ceases for further increase of latitude. For all altitudes above the curve in question, and in particular for all altitudes above sea level, with latitude less than the sea-level critical latitude, there can be no variation of primary intensity with altitude; and, appeal must be made to secondaries for variation of intensity with altitude in these regions. In regions where the primary intensity varies with altitude, that variation must depend upon the energy spectrum of the incoming rays. The type of energy distribution necessary to secure an exponential law is determined. Its form depends upon the law of energy absorption in the atmosphere. Two cases are considered. They correspond to

$$-dE_x/dx = \alpha, \tag{1}$$

$$-dE_x/dx = \alpha + \lambda E_x, \tag{2}$$

where E_x is the energy at the distance x from the top of

* An abstract of a paper which was delivered at the Tercentenary Conference of Arts and Sciences at Harvard University, September, 1936, and published in full in the *Physical Review*, **50**, 1103 (1936).

the homogeneous water equivalent atmosphere, α corresponds to loss by ionization, and λE_x to loss by secondary production. Case (1) leads to an energy distribution which predicts at high altitudes a latitude variation which is enormous and out of all possible harmony with the facts. Case (2) leads to a reasonable high altitude latitude variation. However, the other difficulties concerned with a predicted absence of variation of intensity with altitude in equatorial regions remain.

Combination of Primaries and Secondaries as Measured Entities. The writer generalizes his former theory according to which the primaries produce secondaries in numbers which increase with increase of primary energy. The theory of the soft component is first considered, with (2) as a basis. The energy distribution function, $F(E)$ necessary to give an exponential law for the primaries is of the form $F(E) = B_p/(E + \alpha/\lambda)^p$; and, with this form the absorption coefficient μ_s is $\mu_s = (p - 1)\lambda$. For mathematical convenience the quantity $W = (E + \alpha/\lambda)$, which is nearly the same as E is used throughout for purposes of discussion instead of the true energy E. It is shown that if the number of secondaries n_s accompanying a primary is given by $n_s = \gamma W_x^s$, then below the critical latitude $\mu_s = \lambda s$, and above the critical latitude $\mu_s = (p - 1)\lambda$. If, in accordance with R. A. Millikan's observations we are to have μ_s the same above and below the critical latitude we must have $s = (p - 1)$. If, moreover, μ_s has to have the value 0.5 per meter of water equivalent we must have $s = 1.5$, and so $p = 2.5$ when λ is assigned the value 0.33, which value is determined from the energy for penetration of the earth's magnetic field, 6×10^9 ev., at the critical latitude. The equality of μ_s above and below the critical latitude leads inevitably to an expression for the secondary intensity whose evaluation involves the integration of dW/W between a lower limit which is finite and an upper limit which is infinite unless we assign a finite upper limit E_M, beyond which $F(E)$ is zero. The concept of an upper limit E_M, and so an upper limit of W_M of W is consequently admitted; and, for purposes of illustration the limit taken is $E_M = 5 \times 10^{10}$ ev. The intensity of the secondaries is proportional to $e^{-\mu_s x} \log_e W_M/W_\varphi$ below the

critical latitude, where W_φ is the value of W for penetration of the earth's field at latitude φ. It thus shows a latitude variation. There is also a stronger latitude variation of the primary intensity which, however, does not vary with altitude below the critical latitude. The combined sea-level latitude variation is too great to correspond to the observations and it is necessary to look for the hard component to iron it out.

The Hard Component. A hard component showing no latitude effect when combined with the foregoing contributions to the intensity can be made to provide a satisfactory sea-level latitude variation, a satisfactory ratio of the intensities of the hard and soft components, and a satisfactory increase of latitude effect with altitude through the logarithmic term referred to above. A photon component can therefore fulfill the requirements; but, it is also shown that a charged particle component, operating mainly through its secondaries, will do equally well. Were it not for requirements of variation of latitude effect with altitude, it would be possible to tell the story of both the hard and the soft components as the outcome of the suitably chosen energy distribution in the incoming rays, which rays could then be all of one type. The increase of latitude effect with altitude demands, for the two types of primaries, properties which are different as regards production of secondaries.

Miscellaneous Phenomena. It appears that the average energy of the hard component primaries is determined mainly by the upper limit of their energies while that of the soft component primaries is determined mainly by the lower limit for penetration of the earth's magnetic field. The conditions provided for the hard component secondaries are such that those secondaries completely outweigh the primaries in number; and, this explains why but few very high energy primaries are found in cloud chambers. The higher energy members of the soft component primaries are outweighed by their secondaries but this is not so for the lower energy members. The maximum in the intensity altitude curves shown by Regener's results and by those of the Bartol Research Foundation of the Franklin Institute is attributed to a range phenomena of the secondaries and results from the limitations of the atmosphere. The so-called

secondary hump in the said curves represents the transition which occurs on crossing the critical-altitude critical-latitude curve. The theory provides for the fact that the east-west asymmetry increases with altitude more rapidly than does the total radiation. It provides for such apparently paradoxical conclusions as those resulting from the fact that there is very little asymmetry in shower production in lead, suggesting that showers are produced by hard rays, while shower production increases with altitude more rapidly than the cosmic radiation, suggesting that it is produced by soft rays. The theory in fact makes shower production in lead increase with the energy of the primaries, but provides nevertheless for its rapid increase with altitude in such a manner as to give, at first sight, the impression that it is produced by a soft radiation.

An Alternative Choice of Constants. If one permits a value of λ as large as 0.5, it is possible to provide for $\mu_s = 0.5$ by the assumption that the number of secondaries accompanying a soft component primary is proportional to W_x, or approximately to E_x as assumed in the writer's theory published earlier. This is attended with several advantages; but, necessitates relinquishment of the association between the sea-level critical latitude at 41 degrees and the critical latitude for the soft component. It becomes necessary to assume a second critical latitude phenomenon for the soft component primary, which critical latitude phenomenon does not show itself at all until an altitude of 0.6 meter above sea level is reached. It now becomes necessary to look to the hard component for the sea-level latitude effect. The soft component, however, provides the variation of latitude effect with altitude.

DISINTEGRATION EXPERIMENTS ON THE SEPARATED ISOTOPES OF LITHIUM.*

BY

L. H. RUMBAUGH and L. R. HAFSTAD.

Observations made with targets of 18 micrograms of Li^6 and 200 micrograms of Li^7 under proton and deuteron

* An abstract of a paper published in full in the *Physical Review*, **50**, 681 (1936).

bombardment have given the following results. (1) Two groups of protons with mean ranges of 25.4 cm. and 29.6 cm. air-equivalent are emitted by Li^6 under deuteron bombardment at 540 kv. No group of such range was found for Li^7 under similar conditions. (2) Neutrons are emitted by Li^6 under deuteron bombardment at 300 kv. and above. (3) Short period beta-ray activity was observed from Li^7 under deuteron bombardment at 500 kv. and above with no observable activity from Li^6 under similar conditions. (4) Gamma-rays are emitted by Li^7 under proton bombardment in the neighborhood of 450 kv. and of 1000 kv., with no observable gamma-rays or neutrons emitted from Li^6 with protons of these energies.

STARTING POTENTIALS OF GEIGER-MÜLLER COUNTERS.*

BY

C. L. HAINES.

The starting potential of Geiger-Müller counters filled with various pressures of air, helium, hydrogen, oxygen, argon, and two argon-oxygen mixtures have been accurately determined for counters with oxidized copper cylinders 1.0 cm. in diameter, and bare tungsten wires 0.0075 cm., 0.0125 cm., and 0.025 cm., diameter. Except at low pressures, Werner's equation fits the results fairly well, when suitable constants are chosen, for all these gases except helium. At low pressures, the starting potentials *diminish* as the size of the wire increases.

PUBLICATIONS UNSUITABLE FOR PRESENTATION IN NOTE FORM.†

"Is the Universe Running Down?" by W. F. G. Swann. The Penrose Memorial Lecture delivered before the American Philosophical Society, April 18, 1935. *Proc. Am. Phil. Soc.*, Vol. 75, No. 3, pp. 217–249, July, 1935.

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* An abstract of a paper published in full in the *Review of Scientific Instruments*, 7, 411 (1936).

† These papers do not include those which have appeared in the JOURNAL OF THE FRANKLIN INSTITUTE.

"The New Order of Things," by W. F. G. Swann. A commencement address delivered at the University of Florida, June 10, 1935. The University Record of the University of Florida, Vol. 30, series 1, No. 9, pp. 373–387, Sept. 1, 1935; also published in *Scientific Monthly*, Vol. 41, No. 5, pp. 430–443, November, 1935.

"Nuclear Phenomena and Cosmic-Rays," by W. F. G. Swann. An address delivered at Ohio State University, January 18, 1935, at a special Sigma Xi symposium on "The Nucleus of the Atom and its Structure." *Ohio Jour. Science*, Vol. 35, No. 5, pp. 311–342, September, 1935.

"Report of Investigations Resulting from a Grant Made by the American Philosophical Society to W. F. G. Swann for Furtherance of Work in Nuclear Physics by Himself and his Collaborators," by W. F. G. Swann. Miscellanea, Vol. 1, No. 1, pp. 21–47, September, 1935.

The report comprises a short account of the following investigations, practically all of which have since been published in detail:

A. Investigations Concerning Nuclear Atomic Bursts Produced by Cosmic-Rays.

1. Experiments at various altitudes.
2. Theoretical consequences of the altitude measurements.
3. Further experiments on the dependence of the frequency of cosmic-ray bursts upon the energies of the cosmic-rays.
4. Comparison of burst measurements made with Geiger counters with those made by the use of ionization chambers; and, a study of the relationship between small bursts (showers) and large bursts.
5. Design of apparatus for measurement of atomic bursts in the stratosphere.
6. Development of cloud expansion apparatus and technique.
7. Recording of the paths of nuclear particles from cosmic-ray bursts by the blackening of photographic emulsions.
8. The mutual induction of nuclear bursts.

B. Miscellaneous Problems on Nuclear Physics.

1. The energy spectrum of positrons generated in lead by Thorium C″ gamma rays.
2. The collection of isotopes in large amounts.

"Cosmic-Rays," by W. F. G. Swann. An article written for the opening exercises of the Hayden Planetarium. *Jour. Amer. Mus. of Nat. Hist.*, Vol. 36, No. 3, pp. 255–261, October, 1935.

"Engineering and the New Physics," by W. F. G. Swann. An address given on November 2, 1935, at the University of Pennsylvania at a meeting of the Middle Atlantic Section of the Society for the Promotion of Engineering Education. *Jour. of Engineering Education*, Vol. 26, No. 7, pp. 560–571, March, 1936.

"Biological Effects and Therapeutic Possibilities of Neutrons," by G. L. Locher. The *Amer. Jour. of Roentgenology and Radium Therapy*, Vol. 36, No. 1, pp. 1–13, July, 1936.

"The Use of Geiger-Müller Counters for Locating Radium and for Measuring Gamma-Ray Intensities," by G. L. Locher and J. L. Weatherwax. *Radiology*, Vol. 27, No. 2, pp. 403–407, September 1, 1936.

Cleaning Oil Sands With Hot Air.—L. R. COZZENS. (*Compressed Air*, Vol. 42, No. 7.) When a producing oil well reaches a condition just before the natural rock pressure is entirely exhausted, the modern operator pushes down in the casing a rubber packer, one half inch smaller than the inside diameter of the casing. This packer is forced to the bottom of the casing, and just above the oil sand. The upper end is connected to a gas-engine-direct-driven air compressor. Air, heated under compression to a temperature of 300° F., is forced down the hole. Compression is usually continued for from 48 to 70 hours, or until the air pressure in the pipe at the casing head registers 800 to 1,000 pounds. At this point, the compressor is stopped, and the air is released through a valve in the casing head. The sudden release of air stimulates natural rock pressure which has been forced far back in the sand, and the outrush brings with it into the well reservoir barrels of melted paraffin, wax, and sludge. This residue is promptly removed by a suction bailer and the air pressure is again applied with the result of further improvement in rock pressure. Three or four such treatments may be necessary to restore a well to normal producing volume. In more than 80 per cent. of the wells thus treated, oil production has been increased by from 30 to 50 per cent., and the oil shows a better gravity test, demonstrating that sand channels in the vicinity of the well bottoms are free from damaging residue. The duration of increased production depends of course upon the depth and condition of the sand, but in the majority of cases, a long time may elapse before further air treatments are required.

R. H. O.

NOTES FROM THE NATIONAL BUREAU OF STANDARDS.*

RECENT DEVELOPMENTS OF THE THEORY OF TURBULENCE.

Since the days of Boussinesq and Reynolds more than sixty years ago the theory of the turbulent motion of a fluid has fascinated the minds of scientist and engineer alike. The engineer in his daily experience observed the irregular motion of water in eddying masses and some knowledge of the laws of this motion was a requisite to his professional success. The scientist found the problem a knotty one and some of the foremost intellects of the last half-century have tackled it with indifferent success. Its challenge still stands, and its satisfactory solution still awaits that "happy idea" of which von Karman once spoke, for even the most suitable fundamental concepts have not yet been crystallized.

Recently the attack has turned in a new direction under the leadership of G. I. Taylor, and some understanding of the nature of this new attack should be a possession of every engineer. It has seemed worth while to attempt to survey the situation for those who are too busy with pressing practical engineering tasks to read the ever-increasing literature, which is often highly technical and adorned with much mathematical ornament.

The more recent developments have been stimulated by the intensive development of experimental methods for the study of turbulent flow, in particular for measuring certain statistical properties of the fluctuations of velocity with time. The theory appears to be laying hold of the fundamental phenomena and although it has not yet advanced to the point where it can replace the older empirical methods of attack, the outlook is favorable.

A review of the recent developments, containing a short summary of the basic concepts and a list of 31 papers and books has been prepared by Hugh L. Dryden, chief of the Bureau's Division of Mechanics and Sound, and submitted for

* Communicated by the Director.

publication in the *Journal of Applied Mechanics*, issued by the American Society of Mechanical Engineers.

SUDDEN DISTURBANCES OF THE IONOSPHERE.

Radio transmission at high frequencies is subject to fading, interruption by magnetic storms, and many other vagaries. The most striking of these is an occasional complete disappearance of signals for a brief period, say 15 minutes. This is called a fadeout. It was first recognized as a separate effect in 1935, when it was discovered to occur everywhere on the illuminated half of the globe but not on the night half. It was also discovered that, wherever it occurred, the effect was simultaneous.

This attracted great interest, and a world-wide investigation has since been in progress. It has been discovered that perturbations of the earth's magnetism and of earth currents sometimes occur at the same time as the radio fadeouts. These perturbations are of very different type from the effects occurring during magnetic storms. They are, for instance, small near the poles and great at the equator, just the opposite of magnetic storm effects.

Both the radio and the magnetic effects are at their greatest in that region of the earth where the sun's radiation is perpendicular. They are, for instance, more pronounced where the time is noon than in places where it is some other time of day. A radio fadeout which is observed at a certain place in the morning is most severe and complete for transmissions from the east, and when observed in the afternoon is most severe for transmissions from the west.

The effect is public enemy number one of radio. The disappearance of signals is so complete, in the major fadeouts, that the listener often wonders whether the power has become disconnected or a wire broken. Many an anxious radio operator has dissected his receiving set during a fadeout to try to find out why it went dead. The effect is not as pronounced at broadcast frequencies as at higher frequencies.

A study of the ionosphere, the ionized upper atmosphere, under the direction of J. H. Dellinger, chief of the Bureau's Radio Section, has indicated that a fadeout is due to a very

sudden increase of ionization of a certain region of the ionosphere lying below the recognized layers which reflect radio waves and make long-distance high-frequency transmission possible. Knowledge of the behavior of this region helps to explain some of the facts of radio transmission and is also leading the way to a determination of the causes of fluctuations of the earth's magnetism.

There have been 118 of these fadeouts in the past two years, and in 59 of them an eruption was observed on the sun at the same time as the fadeout. The eruption on the sun sends out a great burst of ultraviolet light, which causes the sudden increase of ionization in the ionosphere, which in turn causes the radio fadeout and the magnetic and earth-current effects. This is leading to increased knowledge of the nature of sunspots and other phenomena of the sun.

Radio fadeouts have thus been demonstrated to be a species of radio interference caused by radiations from 93,000,000 miles away. This effect, while a serious enemy of radio, is proving to be a very good friend of science in studies of the nature of the ionosphere, the processes of radio wave transmission, the mechanisms of terrestrial magnetism, and the phenomena occurring in the sun.

An interesting report of this investigation will be published as RP1016 in the August number of the *Journal of Research*.

INDUSTRIAL USES FOR SILVER.

Previous issues of the Technical News Bulletin have contained references to the investigation by the Bureau and a number of the leading silver producers on the problem of developing new industrial uses for silver. This culminated in the publication of Circular C412 "Silver: Its Properties and Industrial Uses" in October of last year. See Technical News Bulletin 236, p. 113 (December 1936).

Since that time a new project has been started, officially designated as the American Silver Producers' Research Project, having the same general objective as the first investigation, but designed to attack the problem on a much broader front. Fifteen research fellows have been located in nine different institutions, including the Bureau, and are working

on various phases of the problem. At the present time preliminary arrangements have been completed, all the fellowships awarded, funds allocated and the main outlines of the approach decided upon.

As the result of interviews with those in charge of various research organizations many different viewpoints have been considered. It has been decided to follow up each suggestion thus obtained, as well as those offered by members of the technical advisory committee representing the sponsors, in so far as practicable. As the result of careful consideration, a schedule has been decided upon in which each phase of the work has been located at an institution where research of that general character is already under way. The schedule includes studies of argyria, bactericidal properties, chemical properties, fungicidal properties, physico-chemical properties, electro-plating, electrical characteristics, thermal properties, and metallurgical possibilities.

The whole project will be coördinated from the National Bureau of Standards. Since the metallurgical field at present appears the most promising for new uses capable of absorbing a considerable part of the annual silver production, seven of the fifteen men chosen as Research Fellows have been assigned metallurgical problems. Three of these seven have been assigned to the Bureau's Division of Metallurgy, headed by Mr. H. S. Rawdon. The senior Research Associate, A. J. Dornblatt, formerly head of the metallurgy and chemistry section of the U. S. Naval Academy Post Graduate School, will act as the coördinating officer for the entire project so that duplication of work among the different laboratories will be avoided. A considerable portion of his time will be spent contacting industry in order that commercial concerns may be interested in the work being done and to insure that the Project does not duplicate work being carried on in industrial laboratories. Mr. Dornblatt will be assisted by Mr. A. M. Setapen, Research Associate, formerly Teaching Assistant in the Graduate School of the Carnegie Institute of Technology, and by Mr. T. W. Allen, Research Assistant.

Some problems being investigated include the effect of silver additions on the common engineering alloys, development of mechanically superior high silver alloys, charac-

teristics of silver commutators, effects of silver in bearing metals, piston ring inserts of silver or silver alloy, silver soldering irons, characteristics of welding rod containing silver, catalytic properties of silver, heat transfer data on silver and its alloys, optical reflectivity of silver alloys, effect of silver on spore germination, intravenous injection of silver compounds, and electro-deposition of silver alloys.

It is the intention to publish progress reports from time to time in the Technical News Bulletin. It is also desired and planned to coöperate with industry in following up suggestions regarding possible new industrial applications of silver.

RAPID PHOTOMICROGRAPHY.

An apparatus has been constructed by Willard Mutchler and Henry O. Willier of the Bureau's Metallurgical Division, by means of which it is possible to make photomicrographs rapidly. The apparatus, which is now in use at the Bureau, employs roll film or paper, thus dispensing with the repeated loading and unloading of individual film-holders. Some 900 negatives, each 4×5 inches, are secured from a single loading when paper is used. Provision is made for autographing identification symbols on the exposed paper.

A split-beam prism and an auxiliary focusing eyepiece make it unnecessary to remove the holder for purposes of focusing.

The apparatus is being utilized at present to obtain permanent records of the structural effect of corrosion on cross-sections of metallic specimens, approximately 700 micrographs being made per working day. The photomicrographs are taken directly on this bromide-emulsion paper of the usual photostat grades. For many purposes the image on the paper negatives reveals sufficient detail to obviate the need for making prints. Satisfactory prints, however, can also be made from the paper negatives.

WATER RESISTANCE OF PACKAGING MATERIALS.

Moisture-resistant wrappings for bread, cake, potato chips, candy, cereals, tobacco, and a great variety of articles of

commerce that are affected by moisture in the atmosphere, have become so familiar as to be regarded as a matter of course. Rubber and other materials used to protect electrical conductors laid under water, paint and varnish films to protect wood and metal surfaces, aircraft finishes, and gas-cell fabrics in airships are other examples of films and membranes that must be highly resistant to moisture. The effectiveness of these membranes in resisting moisture is the direct result of intense scientific and technical development. One of the most important tools in such development is an adequate method of testing permeability to water vapor.

A survey of the published data on the measurement of the permeability of membranes to water vapor indicates the considerable variety of methods and procedures used and the manner in which recognized variables affect the tests. The study emphasizes the need for correlation of data and standardization of testing methods. Four types of methods, comprising many minor modifications, have been employed. The test period ranged from 2 to 2000 hours; the temperature from $-14°$ to $45°$ C.; the vapor pressure difference from 0 to 72 mm. of mercury; the area of the specimen from 0.15 to 323 cm.^{2}. Considerable individuality has also been exercised in the method of attaching the specimen to prevent leakage, the movement of air in contact with the specimen, the approach to the steady state, and the units of expressing the results. The data have been reported in at least 20 different units.

The data from many sources indicate that the permeability to water vapor of materials commonly used in wrapping and packaging hygroscopic substances ranges all the way from that of waxes, rubber, and varnish films, on the one hand, to that of leather and textiles on the other. The permeability of membranes to air and other gases is no indication of the permeability to water vapor. Rubber, for example, is about 50 times more permeable to water vapor than to hydrogen, and some of the common transparent wrapping materials may be a thousand times more permeable to water vapor than to air.

The data indicate that the amount of moisture that will pass through a membrane is proportional to the area, the

time in the steady-state range, and the vapor pressure difference within certain limits. Some report it inversely proportional to the thickness, while others disagree. A seal to prevent leakage at the edges is considered of the utmost importance. The relative humidity, especially at high values, has a marked influence. The temperature requires close control.

Several mechanisms whereby water vapor is able to pass through many membranes that are almost impervious to air have been suggested. Diffusion in the manner of other gases probably plays a minor rôle. Some believe that the moisture dissolves in the membrane and diffuses in solid solution through it. Others associate the moisture transpiration with the content of hygroscopic moisture, believing the two proportional. Still others attempt to explain moisture transpiration in terms of absorption phenomena, believing that the moisture is absorbed and migrates along internal surfaces provided by the regions of separation between crystallites.

VIBROGRAPH FOR MEASURING THE TRANSMISSION OF VIBRATION THROUGH FRESH CONCRETE.

During the course of studies of the compaction of fresh concrete by vibration it was thought desirable to develop an apparatus for measuring the amplitudes and frequencies of the vibrations within the concrete. An electromagnetic pick-up unit and amplifying unit for use in conjunction with a cathode ray oscillograph have been designed by George L. Pigman, assisted by J. S. Rogers and F. B. Hornibrook, and built at the Bureau for this purpose.

The pick-up unit, inclosed in a rigid, water-tight case, consists essentially of an electromagnet suspended from the case by two springs having a low natural period, and a pick-up coil, rigidly attached to the case, which moves in the air-gap of the magnet. The case (outside dimensions of which are approximately $2\frac{1}{4} \times 2\frac{1}{2} \times 2\frac{1}{4}$ inches) is attached by means of a sime-flexible joint to a metal tube several feet long, through which the lead wires extend. By this arrangement the unit can be used as a probe to pick up the vibration at different positions in a mass of concrete being vibrated. The unit is

designed to respond only to vibrational motion in the horizontal direction.

The signal from the pick-up unit (which is a measure of its velocity of vibration) passes through an electrical integrating unit of the resistance-capacitance type and the signal thus integrated is a measure of the amplitude of vibration. From the integrating unit the signal passes through a three-stage amplifying unit to the oscillograph. A volume control incorporated in the amplifier allows various amplitude ranges to be chosen in such a manner that any amplitude from 0.04 of an inch to 0.00001 of an inch can be made to yield an oscillograph deflection that will extend over at least one-third of the oscillograph scale. Accordingly, measurements of a steady signal can be made over that range of amplitudes within an accuracy of about 3 per cent.

Calibration of the pick-up unit was made by measuring optically the amplitude of the unit placed on a plate made to vibrate near its natural frequency by a rotating eccentric weight. The amplitude ranges below 0.0003 of an inch were not calibrated directly, but were evaluated by means of an electrical calibrating device. This device consists of a voltage divider, operated with alternating current, which gives known output voltages corresponding to actual amplitudes. The evaluation of the amplitude ranges below 0.0003 of an inch was then obtained by extrapolation from the values obtained for the measured amplitude ranges.

The measured value on the vibrograph of a constant amplitude shows a variation of less than 3 per cent. for frequencies ranging from 30 cycles to over 300 cycles per second. This frequency range well covers that of commercial vibrators.

Studies are now being made in the laboratory by F. B. Hornibrook and George L. Pigman of the vibration of concrete with commercial vibrators.

THE FRANKLIN INSTITUTE.

LIBRARY NOTES.

Beginning September fifteenth the library and reading room will be open on Mondays, Tuesdays, Fridays and Saturdays from nine o'clock A.M. until five o'clock P.M., Wednesdays and Thursdays two until ten o'clock P.M. 511 readers made use of the facilities during the twenty-six days of July.

RECENT ADDITIONS.

Architecture and Building.

BOECKH, E. H. Boeckh's Manual of Appraisals. Third Edition. 1937.

Astronomy.

DYSON, SIR FRANK, AND R.v.d. R. WOOLLEY. Eclipses of the Sun and Moon. 1937. International Series of Monographs on Physics.

Automotive Engineering.

Society of Automotive Engineers. S.A.E. Handbook. 1937.

Biochemistry.

NORMAN, A. G. The Biochemistry of Cellulose, Polyuronides, Lignin &c. 1937.

Biography.

POGGENDORFF, J. C. Biographisch-Literarisches Handwörterbuch. Band VI, 1923 bis 1931. 2 Teil. F-K. 1937.

Who's Who in Engineering. Fourth Edition. 1937.

Chemistry and Chemical Technology.

Beilsteins Handbuch der organischen Chemie. Vierte Auflage. Sechsundzwanzigster Band. 1937.

DULAC, ROGER. Industrial Cold Adhesives. A Practical Handbook for the Maker and User. English Edition by Joseph L. Rosenbaum. No date.

EDWARDS, JUNIUS DAVID. Aluminum Paint and Powder. Second Edition Revised and Enlarged. 1936.

EGLOFF, GUSTAV. The Reactions of Pure Hydrocarbons. 1937. American Chemical Society Monographs. No. 73.

KIESER, A. J. Handbuch der chemisch-technischen Apparate. Lieferung 9–10. 1937.

RAWSON, CHRISTOPHER, WALTER M. GARDNER, AND W. F. LAYCOCK. A Dictionary of Dyes, Mordants, and Other Compounds Used in Dyeing and Calico Printing. 1926.

WATERS, WILLIAM A. Physical Aspects of Organic Chemistry. 1936.

Civil Engineering.

BIRD, HAROLD HUGHES. The Practical Design of Plate Girder Bridges. 1920.

U. S. Engineer Department. The Ports of Philadelphia, Pa., Camden, N. J., and Wilmington, Del. Parts 1–2. Port Series no. 4. 1932.

Education.

Minerva Jahrbuch der gelehrten Welt. Zweiunddreissigster Jahrgang. 1937. Abteilung Forschungsinstitute, Observatorien, Bibliotheken, Archive, Museen, Kommissionen, Gesellschaften. 1937.

Electricity and Electrical Engineering.

RAMSEY, A. S. Electricity and Magnetism. An Introduction to the Mathematical Theory. 1937.

SIEMENS-WERKE. Wissenschaftliche Veröffentlichungen. 16 Band, erstes Heft. 1937.

STARLING, SYDNEY G. Electricity and Magnetism for Advanced Students. 1937.

Engineering.

ALLCUT, E. A., AND E. MILLER. Materials and their Application to Engineering Design. 1923.

Hygiene and Physiology.

SURE, BARNETT. The Little Things in Life. The Vitamins, Hormones, and Other Minute Essentials for Health. 1937.

Manufactures.

WATSON, WILLIAM. Textile Design and Colour. Elementary Weaves and Figured Fabrics. Fourth Edition with Appendices on the Manufacture of Rayon (Artificial Silk) and Standard Yarns, Weaves and Fabrics. 1937.

Metallurgy.

FRIEND, J. NEWTON. Iron in Antiquity. 1926.

Osmond, Floris. The Microscopic Analysis of Metals. Edited by J. E. Stead. Third Edition, Revised and Corrected by L. P. Sidney. 1924.

Mining Engineering.

MOSS, K. NEVILLE. Gases, Dust and Heat in Mines. 1927.

Pharmacy.

American Pharmaceutical Association. Pharmaceutical Abstracts. Volumes 1–2. 1935–1936.

Physics.

HOUWINK, R. Elasticity, Plasticity and Structure of Matter. With a chapter on the Plasticity of Crystals by Dr. W. G. Burgers. 1937.

LORENTZ, H. A. Collected Papers. Volumes 1–4, 7–8. 1934–1937.

Rutherford, Ernest 1st baron. The Newer Alchemy. 1937.

Willey, E. J. B. Collisions of the Second Kind: their Role in Physics and Chemistry. 1937.

Scientific Papers.

NORTHRUP, EDWIN FITCH (pseud. Akkad Pseudoman). Zero to Eighty: Being my Lifetime Doings, Reflections, and Inventions, also my Journey Around the Moon. 1937.

BOOK REVIEWS.

PHYSICAL ASPECTS OF ORGANIC CHEMISTRY, by William A. Waters. 501 pages, illustrations, 14 × 22 cms. New York, D. Van Nostrand Company, Inc., 1936. Price $9.50.

The "new physics" which had its beginnings about the period of the Great War caused upheavals in the conservative and set conceptions in many fields. The physical conceptions of atomic and molecular structure that emerged from this period were startling and they opened the door to much work in the way of orienting the existing thought in other sciences which were based upon these conceptions. Not only this, but they helped toward settlement of controversies of many years standing.

This book is a survey of a rather wide range of chemical theories with relation to this matter. In the first chapter, on chemical affinity, there is told of the struggle between the unitary and dualistic theories which was carried on for nearly a century between inorganic and organic chemists, and how this was resolved in modern work by modern knowledge. Physical theories of molecular structure are then discussed including ionization of molecules, polarization of molecules and ion-pairs, and intramolecular ionic charges. The third chapter, on valency, takes up the threads left from the first chapter from the point after the treatment on the two principal types of valency, that is, the first which is dependent on electron transfer and the second depending on electron sharing. It describes some of the variants on these principal types that have been suggested from time to time, including the mixed or semi-polar bond, the dative bond or coördinate link, the hydrogen bond, odd electron bonds, bivalent carbon, and the oxygen bond.

From here the author launches his treatment into the subjects of electrical dipoles, free radicals and their non-ionic reactions, the reactivity of halogen compounds, hydrolysis and esterification, ionotropic change, and conjugation. The historic aspect is kept continually in view throughout the book and, necessarily, there is much reference made to the work of others. These are listed at the bottom of various pages and in an author index.

The developments outlined in the book are by no means conclusive. There are many that, today, are open to criticism. But the review of the past leading up to the present position is opportune. In view of an indicated novel type of organic chemistry being developed in which the course of a reaction is traced back to the electrical properties of the molecule and ultimately to the electronic structure of the component atoms, this book should prove informative to chemical technologists.

R. H. OPPERMANN.

AN OUTLINE OF ATOMIC PHYSICS, by members of the Physics staff of the University of Pittsburgh: Oswald H. Blackwood, Elmer Hutchisson, Thomas H. Osgood, Arthur E. Ruark, Wilfred N. St. Peter, George A. Scott and Archie G. Worthing. Second Edition, 414 pages, illustrations, 15.5 × 23.5 cms. New York, John Wiley & Sons, Inc., 1937. Price $3.75.

As those familiar with the first edition of this book are aware, the object of the authors was to present a volume on atomic and molecular physics which steered a middle course between the difficult mathematical treatise on the one hand, and the unsatisfying "popular" work, on the other hand. In this aim the authors have been successful, and a second edition of the book is entirely justified.

In revising the book preparatory to the second edition, a questionnaire was sent out, which was returned by more than 80 per cent. of those to whom it was sent. The answers were very helpful in pointing out errors, in showing the relative use of the different chapters and in suggesting additional subject matter. Most of the chapters have been changed, either to improve the clarity or to introduce new material. A new chapter has been added on neutrons, positrons and nuclei.

Although the book requires of the reader only elementary mathematical preparation, it does succeed in giving him a clear picture of atom mechanics, insofar as present day knowledge extends. It is excellent as preliminary study for those intending to go further in science, and is equally fitting for those aiming toward other professions.

It seems to the writer that an occasional judicial use of the calculus would have assisted greatly in some of the presentations, without unduly straining the capacity of the reader. Also, he would like to have seen a little more on Schrödinger's equation, although the basic principles of wave mechanics are explained in a clear cut manner. However, this might be a purely personal reaction on the part of the reviewer. Certainly the book accomplishes what it is intended to accomplish. What more can we ask?

The book is excellently printed and bound, and is replete with illustrations of excellent quality and many references. It is a credit to its producers.

GEORGE S. GARDNER.

IONS IN SOLUTION, by R. W. Gurney. 203 pages, illustrations, 14.5 × 22.5 cms. Cambridge, University Press, 1936. Price $3.00.

The author, in his book published in 1934, "Elementary Quantum Mechanics," has treated the problems of quantum mechanics by graphical methods, using energy diagrams to a considerable extent. That his treatment was successful in helping many readers to an understanding of quantum mechanics to which they might not otherwise have attained is shown by the worn condition of the book in the Franklin Institute Library.

In an analogous manner, the author has given us a picture of ionic processes in this recent book "Ions in Solution." Energy diagrams, as previously, play an important part. He has covered the field of ionic behaviour in a thorough and painstaking manner, including some discussion of experimental methods. His treatment is refreshing and the book is not too long, a very attractive feature.

The binding is not particularly sturdy, although the printing is good. We would recommend this book to anyone desiring to obtain fundamental knowledge of solution processes.

GEORGE S. GARDNER.

ALUMINUM PAINT AND POWDER, by Junius David Edwards, second edition, 216 pages, 16 × 23.5 cms. New York, Reinhold Publishing Corp., 1936. Price $4.50.

In the Preface of this book, it is stated that this is the second edition, the first having been published only nine years ago. The indication is that the use of aluminum powder has been increasing to such an extent that the first edition is out of date. Evidence of the increasing use is not difficult to find, for a much larger number of structures can be seen coated with aluminum than was the case a

few years ago. It is stated that the new edition is, in fact, a new book; and even though it is more than double the length of the first edition, many subjects of interest have had to be briefly discussed, or in some cases, omitted for lack of space.

The author tells us how aluminum powder is manufactured—the stamping operation and polishing, about the Hall process and the Hametag process, and then some information on grained and granulated aluminum. In discussing the properties of aluminum powder, very interesting illustrations are given showing its microscopic appearance and reference is made to a bibliography of the Mellon Institute on its non-toxicity. There is given very useful information on the preparation of aluminum paste and powder for use as a paint including various vehicles used and vehicle characteristics. As a protector of metals it is said that while originally used on iron and steel, the application of the paint has been extended to the coating of aluminum, magnesium, galvanized iron and other metals. As a protector its principle value lies in providing a tough, protecting coat of long life and high resistance to moisture penetration.

Some special properties and uses of the paint include visibility, emissivity and opacity and these are discussed with relation to various structures. As a protector of wood, various tests are cited and explained. It is shown that aluminum powder is also used for many other purposes such as in printing, coating of paper, coating of balloon fabrics, the manufacture of fireworks, and aerated concrete, to mention a few.

The book is well written and interesting. Its contents as a whole should be valuable for immediate use by only a few. Its breadth of coverage however makes for use by a larger number—these being interested in certain portions of the book. The subject index helps considerably in this latter respect.

R. H. OPPERMANN.

ZERO TO EIGHTY, BEING MY LIFETIME DOINGS, REFLECTIONS, AND INVENTIONS; ALSO MY JOURNEY AROUND THE MOON, by Akkad Pseudoman (Edwin F. Northrup). 283 pages, plates, illustrations, 16 × 24 cms. Princeton, New Jersey, Scientific Publishing Company, 1937. Price, $3.00.

Zero to Eighty is a story of imagination, written in the year 2000 A.D. Narrated in the first person, it is a review of the achievements of an eighty-year-old individual, a Mr. Akkad Pseudoman. The use of the name itself suggests an imaginative individual of fiction, and creates curiosity as to the reason for its assumption. This is quickly explained in the Preface. It permits the generation of greater interest from a greater number of readers and at the same time presents in a fascinating manner certain scientific material that cannot fail to be understood. The real author of the book is E. F. Northrup, an engineer well known in the fields of scientific instruments and industrial furnaces.

The early life of Akkad Pseudoman was one under very favorable circumstances. His father and mother both seemed to be well adapted for his mental training, which resulted on arrival into manhood of an unwavering fixation of purpose. This was indeed a virtue, especially when coupled with other worthy possessions. Upon this foundation and the good fortune of true, honest and like-minded friends there is evolved a life of invaluable service to humanity. Adventure, action, and success, give color to the story. Early in Pseudoman's life he discovers by accident an ancient Apache gold mine in Arizona which helps to furnish the means for the development of an electric gun and his ambition to circle

the moon in a rocket ship. The perfection of the former required many years of toil together with a lifelong friend, Jean Bizet. The accomplishment of the latter, which is the climax of the story, required a similar additional time. There is a kidnapping in the story and a shipwreck as well as experiences in stratosphere transportation. In fact, the book is so well rounded that readers of widely diversified likes and dislikes will find much to carry on their interest.

The electric gun consists of a series of coils of copper tubing in single layer energized with an electric current of a frequency of around 6000 cycles in polyphase. The projectile, stream-lined, passes through the coils at a very high velocity. It becomes applied to many uses aside from strictly military purposes. Finally in a very much enlarged form it is used to shoot the specially constructed rocket ship into space through the gravitational pull of the earth. The rockets then propel and steer the ship around the moon and back to earth. Technical details of these apparatuses are not contained in the story. They are given in a technical supplement so as not to interfere with the even flow of interest.

The style of writing is fascinating and the construction of the story is well done. It may be said, however, that the narrative contains too many successes and does not stress the overcoming of seemingly insurmountable difficulties. Also some trouble may be encountered by the non-scientifically minded reader in envisioning the metric system of weights and distances which are used instead of the English system. But these, of course, are of minor consequence.

This book was written for the layman. It is a thrilling story of ambition, adventure and accomplishment. It undoubtedly will be in popular demand.

R. H. OPPERMANN.

EARLY SCIENCE IN CAMBRIDGE, by R. T. Gunther. 513 pages, plates, illustrations, 14.5 × 22 cms. Oxford, The University Press, 1937. Price 2.2.0.

Fourteen years ago Dr. R. T. Gunther, Fellow of Magdalene College, Oxford, and Curator of the Oxford Museum of Science, gave to the scientific world and students of the history of science, his first volume of *Early Science in Oxford*, since which time ten volumes of that interesting subject have appeared, together with two quarto volumes on *The Astrolabes of the World*, as well as numerous articles appearing in scientific magazines. Now Dr. Gunther has brought forth his new work, which evidently was conceived with the idea of waking up Cambridge—as he did years ago at Oxford—to the fact that they, too, have a mass of material pertaining to the sciences of times gone by. These have been scattered throughout the various colleges and tucked away in obscure places until brought to light by this energetic student of the history of science and a plea made that the Cambridge authorities might institute their own Museum of Science.

This interesting work will indeed be valuable to all lovers of antiquities, especially in the field of science, for the book is replete with illustrations of the many treasures to be found at Cambridge. The seventeen chapters and five appendices cover such subjects as mineralogy, geology, botany, zoölogy, anatomy, medicine, chemistry, astronomy, mathematics, etc. All are of interest to present-day students. There is much biographical data on the early scientists of Cambridge, together with many amusing incidents of their lives. The Abbot of St. Albans, Richard of Wallingford's account of his Rectangulus (c. 1326) is illustrated and commented upon. The chapters on astronomical instruments, sun-dials, ring-dials, astrolabes and orreries, is like the work on Oxford's treasures,

unsurpassed, and should interest many. Among the many amusing incidents recited, is one of interest to Philadelphians. On May 25, 1822 the following notice was put up in the town of Cambridge:

> "Zachariah Whitmore of Philadelphia, North America, begs to inform the inhabitants of Cambridge that he intends starting from Lynn on his Water Velocipede at 12 o'clock, and will arrive at Cambridge between 6 and 7 o'clock in the evening on Whit Monday next."

About 2,000 people assembled at the appointed time and after waiting several hours discovered the notice was a hoax and retired to their homes.

Dr. Gunther having done so much in instigating the establishment of the Old Ashmolean Museum at Oxford for their historical scientific collections deserves unstinted praise in what he is now trying to do for Cambridge. We wish him and others there continued success.

The book, bound in light blue cloth and well indexed, should be on the shelves of every college library and scientific society of the country.

HARROLD E. GILLINGHAM.

ELASTICITY, PLASTICITY, AND STRUCTURE OF MATTER, by R. Houwink. 376 pages, plates, diagrams, 14 × 22 cms. New York, The Macmillan Company, 1937. Price $6.00.

Much work has been and is being done on this subject and there have resulted many improvements in existing materials and discoveries of new materials. A bird's-eye view of the subject indicates that the possibilities for new products and applications of them are very great. The layman does not have to look far to see such materials in use that only a few years ago were non-existent. With increasing frequency there appear reports of something new. Therefore the impression made is that fundamental research is attacking the subject on a broad united front with the present amazing results.

The author of this book, in the foreword, states that in the literature of the subject, a unity of thought between workers in various fields is seldom encountered. One of his tasks in this work then, is to trace such a unity as far as it is possible at present. An examination of the laws assumed to hold for deformation is given as well as observations on the degree of divergence from these laws. To be able to prophecy about the behavior of a material upon the deformation on the basis of its structure, is in the opinion of the author the key to deliberate synthesis of materials with definite desired elastic and plastic properties.

The book starts with a survey of elastic and plastic deformations in general. References are made to methods of measuring elasticity, plasticity and viscosity. Then there follow general remarks about the internal structure of matter in relation to its elastic and plastic behavior, the formation of solid matter from a fluid, and the conditions for the elastic and plastic behavior of matter.

A chapter of the book entitled "Plasticity of Crystals" is presented by W. G. Burgers. In this chapter a general description is given of the principal phenomena occurring on plastic deformation of crystalline substances with particular attention to the differences in plastic behavior existing between these substances and those which can be considered as truly or partly amorphous.

The rest of the book, which is the larger part, is devoted to a comparison with each other of very different substances. Glass, resins, and asphalt as certain typical examples are treated together as amorphous substances from which an

analogy can be made in the case of similar materials. Natural and synthetic rubbers are taken up as is cellulose and its derivatives, which are in general formed by the esterification or etherification of some of the OH groups of cellulose. Then proteins, paints, clay and sulphur are discussed.

The book is a very interesting exposition of the present situation and goes far toward the making of a common language and basis of thought among workers in diversified fields.

R. H. OPPERMANN.

FUNDAMENTALS OF ENGINEERING ELECTRONICS, by William G. Dow. 604 pages, illustrations, 15 × 23 cms. New York, John Wiley & Sons, Inc., 1937. Price, $5.00.

Probably the best reason for a thorough understanding of the fundamentals of this subject is ably given in the Preface. The exact words are as follows: ". . . No matter how facile an engineer may be in the manipulation of electronic circuits, his effectiveness is distinctly limited unless he has a satisfactory understanding of the operating principles of the electronic circuit elements that he uses." Just to what extent this is true probably could never be measured. One reason for this is that few ever know the difficulty and the very strenuous work to overcome it that such an engineer must and does do to master a situation. If young engineers were to take heed of the advice of thoroughly understanding fundamental principles in this rapidly growing field, much time saving could be accomplished.

The book generally is divided into two parts. The first, under the heading of electrons, is divided further appropriately so that the study of electrons is quite thoroughly covered. At the beginning preparation is made for and analysis presented of the electrostatic field within a triode before any electrons are released or when the number of escaping electrons is so small that their charges and movements have little effect on the electric and magnetic fields. This establishes the nature of the dependence of the space-charge-free off-cathode gradient on plate and grid voltages, and the dependence of the tube current after electron release on the off-cathode gradient before release. These two studies are subsequently combined to show why the current-voltage relationship must be of the type of the characteristic curves for a triode. Studies are made of the principles that govern electron movements in the presence of electric and magnetic fields, of space-charge flow in four and five electrode tubes, and of the principles underlying thermionic emission. The first part of the book is concluded by divisions devoted to the applications of high vacuum thermionic tubes, chiefly in amplifier circuits.

Part II is entitled "Electrons, Atoms, and Radiation." Atomic energies and energy levels for particular elements are topics which lead to an insight to the types of electronic behavior that involve interactions between electrons, atoms, and electromagnetic radiation. Photoelectric and gaseous discharge theory and application are then treated. There is a separate chapter on mercury vapor rectifiers.

The author wastes no space in his work for anything not directly in line with the subject. The work is an intensive study and should not be used except by those thoroughly prepared. It is not, by any means, to be classed with "easy reading." As a text for prepared students and as a reference work for engineers who are conversant with the subject in no small degree, the book should prove valuable.

R. H. OPPERMANN.

SOUND, A TEXT BOOK, by Arthur Taber Jones. 450 pages, illustrations, 15 × 22 cms. New York, D. Van Nostrand Company, Inc., 1937. Price, $3.75.

In very recent years the subject of acoustics has assumed considerable importance. This was partly due, first, to the need of a knowledge of acoustics to accomplish a very much desired result, and second, to the very obvious beneficial results at first obtained. Interest in the subject of sound, however, goes back through many centuries. From its first conception to the present day interest has risen and fallen. Today sound is employed in many new ways and consequently interest is quite keen.

The author of this book has endeavored to present a work that is simple and conclusive. Only a meager knowledge of physics and mathematics, together with a desire to learn is necessary to study it. First of all there is given the necessary explanatory matter on sound and its characteristics, and the definitions of various kinds of sound. Then the production of various noises is discussed such as the explosion of a fire cracker, thunder, and sounds from liquid drops and bubbles. Vibratory motion producing musical sounds leads to treatments on simple tones and combinations of tones, and musical scales. In a chapter on transmission of sound there is a very interesting part devoted to reflection, interference, diffraction and scattering.

A feature of the book especially noteworthy is the pointing out that all is not known in regard to the subject generally and in many subdivisions. One place where this occurs is with relation to audition and the anatomy of the ear. The author states that there is considered some "theories which *attempt* to explain the facts" and he follows through in good form in his explanations.

With relation to speech and song there is much interesting information from a scientific angle. Here, there is a very good illustration of the author's skill in exposition in an impressionable manner. The reference to simple, every-day observations is coupled with the gist of what he means to implant so that understanding is facilitated. The final part of the book is devoted to the applications of sound such as talking motion pictures and fog signals as well as the reduction of sound.

Throughout the book, at what seem to be appropriate places there appear questions on what has gone before. The approach to the various topics is often through the historical although this is not always followed.

The book is a good text on the fundamentals of sound.

R. H. OPPERMANN.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS.

Report No. 591. An Analytical and Experimental Study of the Effect of Periodic Blade Twist on the Thrust, Torque, and Flapping Motion of an Autogiro Rotor, by John B. Wheatley. 7 pages, illustrations, tables, 23 × 29 cms. Washington, Government Printing Office, 1937. Price ten cents.

An analysis is made of the influence on autogiro rotor characteristics of a periodic blade twist that varies with the azimuth position of the rotor blade and the results are compared with experimental data. The analysis expresses the influence of this type of twist upon the thrust, torque, and flapping motion of the rotor. The check against experimental data shows that the periodic twist has a

pronounced influence on the flapping motion and that this influence is accurately predicted by the analysis. The influence of the twist upon the thrust and torque could be demonstrated only indirectly, but its importance is indicated.

Report No. 593. Cooling of Airplane Engines at Low Air Speeds, by Theodore Theodorsen, M. J. Brevoort and George W. Stickle. 10 pages, illustrations, 23 × 29 cms. Washington, Government Printing Office, 1937. Price ten cents.

A comprehensive experimental study has been carried out at full scale in the N. A. C. A. 20-foot wind tunnel, the general purpose of which is to furnish information in regard to the functioning of the power plant and propeller unit under different conditions. This report deals particularly with the problem of the cooling of an airplane engine on the ground. The influence of different nose forms, skirts, flaps, propellers, spinners, and special blowers has been investigated. Among the more interesting results are the demonstration of the comparative inefficiency of adjustable skirt flaps, the detrimental effect of small-diameter front openings of the cowling, and the very beneficial effect of a carefully designed airfoil section near the hub of the propeller. A small axial fan of simple construction was found to give efficient cooling on the ground.

Report No. 595, Full-Scale Tests of a New Type N. A. C. A. Nose-Slot Cowling, by Theodore Theodorsen, M. J. Brevoort, George W. Stickle, and M. N. Gough. 9 pages, tables, illustrations, 23 × 29 cms. Washington, Government Printing Office, 1937. Price 10 cents.

An extended experimental study has been made in regard to the various refinements in the design of engine cowlings as related to the propeller-nacelle unit as a whole, under conditions corresponding to take-off, climb, and normal flight. The tests were all conducted at full scale in the 20-foot wind tunnel. This report presents the results of a novel type of engine cowling, characterized by the fact that the exit opening discharging the cooling air is not, as usual, located behind the engine but at the foremost extremity or nose of the cowling. This type of cowling is inherently capable of producing two to three times the pressure head obtainable with the normal type of cowling because the exit opening is located in a field of considerable negative pressure. Thus identical conditions of cooling can be obtained at correspondingly lower air speeds. In general, the efficiency is found to be high, owing to the fact that higher velocities may be used in the exit opening. Flight tests of a temporary installation showed promising results.

PHYSICS IN INDUSTRY, by K. T. Compton, E. C. Sullivan, Zay Jeffries, E. Q. Adams, Paul D. Foote, J. P. Den Hartog, John Ely Burchard, Oliver E. Buckley, Clark B. Millikan, Joseph Slepian, Homer L. Dodge and A. R. Olpin. 290 pages, plates, illustrations, 13 × 20 cms. New York, The American Institute of Physics. Price $1.50.

"In the last fifty years physics has exerted a more powerful beneficial influence on the intellectual, economic and social life of the world than has been exerted in a comparable time by any other agency in history." This statement Professor Compton justifies by reference to the ramifications of the science of physics and the contributions to knowledge, industry and the art of living which have come from them. Like K. K. Darrow in his recent book, "The Renaissance of Physics,"

Compton offers some explanations why the scientist bearing the cacophonous label of physicist enjoys so little popular recognition.

But "Physics in Industry" is not primarily a recitation of past accomplishments of physics. Its writers are most vigorous when dealing with the challenges of the present. H. G. Wells has said, "The main difference of modern scientific research from that of the middle ages lies in its collective character." Contemporary scientific research is continuing this tendency by accepting new social responsibilities. This has been exemplified recently by the plans of the International Council of Scientific Unions, representing twenty countries, to examine the results of physical, chemical, and biological sciences with reference to their practical application in the life of the community. In academic centers there has arisen a more articulate interest in industrial physics and more explicit discussion of the training of physicists for industry.

Of the twelve contributors to this volume, six would be classed as physicists, while others represent related fields. All have had teaching experience. Each writes of the problems currently being solved by physics in his industrial field, whether that be one based upon ancient art or one growing directly from modern research.

The fields in which the role of physics is outlined are: the glass, metal, petroleum, building, communications, aeronautical and electric power industries. There is an especially interesting chapter on problems of vibration in industry. The chapter on building contains an unbiased discussion of the limitations of prefabrication, and is insistent on the challenge which the building industry offers to physics for more adequate work on the vital problems of housing. The final two chapters are on the training of physicists for industry, giving respectively the views of the educator and the employer. Dean Dodge has outlined an ideal curriculum in industrial physics and discussed the extent to which this program is realized in various American universities.

"Physics in Industry" is characterized by consistent emphasis, lucid writing and interesting illustration. It may be highly recommended to one desiring a perspective of the part physics plays in modern life. The chapters on physics education should be of particular interest to students and to educators concerned with vocational guidance.

R. L. WEBER.

A TEXTBOOK OF ORGANIC CHEMISTRY, by Hugh C. Muldoon. Second Edition, 590 pages, illustrations, 14 × 21 cms. Philadelphia, P. Blakiston's Son & Co., Inc. Price, $3.00.

Those who are familiar with the first edition of this book are well acquainted with the manner in which the material is presented. This, the second edition, however, is revised to a considerable extent, not in the manner of presentation, for that remains as an inseparable trait of the author, but in the arrangement and content of the book. The result is a text of unusual merit.

The work is directed to students who desire to follow medicine and pharmacy. It is therefore limited to this extent, and while a general coverage of the subject is attempted, there are many important instances where a more thorough or complete treatment may be advisable for students desiring to follow other than these two fields.

Beginning with an introductory chapter wherein there is given basic information as a starting point, the author gives a remarkably understandable treatment

of the underlying principles and important facts of the science. It is a beginners' text and as such the approach to each topic reveals a good knowledge of the beginner's viewpoints and difficulties.

At the end of the book there is a glossary of medical terms and a subject index. For the purpose for which it is intended this book is well suited.

R. H. OPPERMANN.

PUBLICATIONS RECEIVED.

Technological Trends and National Policy, Including the Social Implications of New Inventions, Report of the Subcommittee on Technology to the National Resources Committee. 388 pages, illustrations, tables, 23 × 29 cms. Washington, Superintendent of Documents, 1937. Price, $1.00.

Theory of Alternating-Current Machinery, by Alexander S. Langsdorf. First edition, 788 pages, illustrations, 16 × 23.5 cms, New York, McGraw-Hill Book Company, Inc., 1937. Price $6.00.

Textbook of Thermodynamics, by Paul S. Epstein. 406 pages, illustrations, tables, 16 × 23.5 cms. New York, John Wiley & Sons, Inc., 1937. Price $5.00.

Carl Friedrich Gauss, Inaugural Lecture on Astronomy and Papers on the Foundations of Mathematics, Translated and Edited by G. Waldo Dunnington. 91 pages, illustrations, 14 × 20 cms. Baton Rouge, Louisiana State University Press, 1937. Price, $1.00.

Physics in Industry, by K. T. Compton, E. C. Sullivan, Zay Jeffries, E. Q. Adams, Paul D. Foote, J. P. Den Hartog, John Ely Burchard, Oliver E. Buckley, Clark B. Millikan, Joseph Slepian, Homer L. Dodge and A. R. Olpin. 290 pages, plates, illustrations, 13 × 20 cms. New York, American Institute of Physics, 1937. Price, $1.50.

Home-Radio Pocket Trouble Shooter "Gadget," by Alfred A. Ghirardi. 18 pages, 13 × 18 cms. New York, Radio & Technical Publishing Company, 1937. Price $.50.

Auto-Radio Pocket Trouble Shooter "Gadget," by Alfred A. Ghirardi. 24 pages, 13 × 18 cms. New York, Radio & Technical Publishing Company, 1937. Price $.50.

National Advisory Committee for Aeronautics. Twenty-second Annual Report, 1936, including Technical Reports, Nos. 542 to 576. 574 pages, illustrations, tables, 24 × 30 cms. Price, $2.50. Technical Notes No. 604, Full-Scale Wind-Tunnel and Flight Tests of a Fairchild 22 Airplane Equipped with External-Airfoil Flaps, by Warren D. Reed and William C. Clay. 17 pages, illustrations. No. 605, Noise from Propellers with Symmetrical Sections at Zero Blade Angle, by A. F. Deming. 11 pages, illustrations. No. 606, Empirical Corrections to the Span Load Distribution at the Tip, by H. A. Pearson. 16 pages, illustrations. No. 607, The Behavior of Thin-Wall Monocoque Cylinders under Torsional Vibration, by Robert E. Pekelsma. 14 pages, illustrations. 4 pamphlets, 20 × 26 cms. Washington Committee, 1937.

Bell Telephone Laboratories, Monographs: B-977, Organic Finishes—Effect of Film Thickness, by A. E. Schuh and H. C. Theuerer. 15 pages, illustrations, tables. B-999, Moisture in Textiles, by Albert C. Walker. 20 pages, illustrations, tables. 2 pamphlets, 15 × 23 cms. New York, Bell Laboratories, 1937.

CURRENT TOPICS.

Dry Ice From Flue Gas.—D. H. KILLEFER AND J. WELLFORD MARTIN. (*Power*, Vol. 81, No. 8.) The cost of recovery from the flue gas of power plants of CO_2 gas in the very high purity essential for conversion to a solid has been prohibitive. But a new method for recovery in ample quantities at a favorable cost offers much promise. It is known as the Macmar Process and is now in full plant scale operation at 15 tons daily capacity. The process is similar in many respects to the alkali process usually employed and the equipment used is practically the same. After the flue gas is washed to remove sulphur dioxide, dust and soluble impurities, it is passed through a series of three packed towers or absorbers. In the second tower of this series is pumped hot potassium carbonate lye, and ammonia is added as required to give a substantial concentration in the gas mixture. Either anhydrous or aqua ammonia may be used. The lye from the base of this tower is cooled below 100° F. and pumped into the top of the third or gas exit tower. From there after being reheated it is pumped to the top of the first or gas entrance tower. From the bottom of the first tower the lye carrying CO_2 in solution as bicarbonate is pumped into a lye boiler where CO_2 is released by heat. Any of the usual methods of compression, refrigeration and pressing may be used after the gas has been purified. Flue gas mixtures containing as little as 8 to 13 per cent CO_2 may be processed.

R. H. O.

Apparatus for Demonstrating Electrical Ignition of Mine Gas.—Many people consider the mining of coal to be an extremely hazardous occupation; but it should be remembered that most large industries have to meet special conditions, which if not dealt with properly might become hazards to life and property. In endeavoring to help the coal mining industry to prevent accidents and disasters, the U. S. Bureau of Mines has engaged in a program of education on conditions and practices that must be avoided. An effective way to teach safety is by visual demonstration. In the U. S. Bureau of Mines Information Circular 6944, E. J. GLEIM describes a type of demonstration apparatus installed in the electrical laboratory of the Bureau's Pittsburgh Experiment Station. In this apparatus the demonstration takes place in a glass chamber of the form of a cylinder 7 inches in diameter and 12 inches in height. On the top there is a 5½ inch circular opening sealed with waxed paper. An

explosive mixture of gas is made within the chamber by admitting natural gas of the proper amount and the pressure is equalized with the atmosphere outside. Various types of hazard are represented in the chamber, such as the striking of an electric arc in various ways that might occur in a mine. The electric arc, of course, sets off an explosion of the gaseous mixture in the chamber and the waxed paper over the circular opening bursts and releases the expanding gases before enough pressure can develop to strain the glass wall.

R. H. O.

Heat to Disperse Fog at English Airports.—(*Heating and Ventilating*, Vol. 34, No. 8.) The prospect of applying heat to the dispersal of fog over airports and to assist in the propulsion of high-speed airplanes is mentioned in the report of the British Aeronautical Research Committee, which was recently published. The growth of air traffic has raised the question of fog dispersal, and costly though it is likely to be, it may be worthy of further investigation. The demand is for a system which will keep a space 250 yards long, 100 feet wide, and 300 feet deep clear for a period of 5 minutes. The committee believes that the process is not impracticable and as a result experimental heating plants for fog and mist dispersal purposes may be installed at various British airports in the near future.

R. H. O.

Liquid Mud Lifts Ship.—H. CHAMBERLIN. (*Engineering News Record*, Vol. 119, No. 6.) Liquid mud substituted for water in a cofferdam was used to raise a 2,000 ton ship 9 feet above water in Miami harbor, Florida. Lying along shore, the ship was enclosed in a cofferdam, utilizing the shore as one side. The normal draft of the ship was 15 ft. and it was decided to raise her an additional 3 ft. by reducing her draft to 12 ft. Since the vessel was without machinery or cargo and could be lightened only to an inconsequential extent, it was determined to float her in a fluid of greater specific gravity than water. This was accomplished by using fine liquid mud which weighed 165 lb. per cu. ft. compared with the weight of salt water, which is about 65 lb. per cu. ft. Every day, as the water inside the cofferdam was displaced by mud, the ship rose. Cables run from her mast held her on even keel, but she floated trim just as if she were in her natural element. At night, when the agitated mud settled, the ship would drop back part of the distance gained, but when the mixture was stirred up with water jets the following day and more mud was pumped in, the vessel would rise again. Finally sand and gravel were forced under her keel and she was held at the desired height. Not a plate in her hull had been strained or cracked.

R. H. O.

World's Oldest Bathroom Built 5,000 Years Ago.—(*The Valve World*, Vol. XXIV, No. 3.) The idea of a separate room in the house for bathing purposes is 5,000 years old, says the Plumbing and Heating Industries Bureau. The Oriental Institute of the University of Chicago has excavated in Iraq, once ancient Babylonia, a room 15 feet square in the palace of King Urninmar. The room has a floor of water-proof bitumen with a drain made of clay tile. Here the king stood while slaves threw water over him. The fact that the room was built three thousand years before the beginning of the Christian era is established by the imprint of the name of the king on all of the bricks used in the construction of the palace.

R. H. O.

Revised Method For Determining Dripping Points of Lubricating Greases.—W. W. NIVEN, JR. (*National Petroleum News*, Vol. XXIX, No. 30.) There is no standard method for determining the characteristics of greases when subjected to high temperatures. They do not exhibit true melting points but rather a gradual change from the solid to the liquid state. This change may be attributed partly to the breaking away of the mineral oil from the soap and partly to the liquefaction of the soap constituent. Comparison of various "melting point" methods led to consideration of the Ubbelohde method and a revision of this was made to fit certain types of grease to be tested. The grease is contained in a Pyrex tube, in the bottom of which is a 3 mm. orifice. A thermometer bulb is inserted in the grease. As a heating bath a 400 ml. beaker containing about 300 ml. of glycerine is heated to a temperature 50 deg. above the anticipated dripping point of the grease and maintained at this point. The dripping point of the grease is taken as the temperature at which the first drop of mineral oil falls from the orifice. The method gives results which are in accord with practice.

R. H. O.

The Absorption System Comes Back.—S. RUPPRIGHT. (*Refrigerating Engineering*, Vol. 34, No. 2.) Until not long ago, few refrigerating engineers were interested in temperatures of −40 deg. F. and below, because their use was considered economically justifiable only in rare cases such as in chemical processes where the margin of profit obtainable permits employing costly means. The compression machine has generally met the needs satisfactorily. In Europe, however, the absorption machine was not abandoned to the extent that it has in this country. It survived a period of little progress in design on the merit of its being a waste steam utilizer. As far back as 20 years ago the way was pointed for improvement in

this type of machine. Dr. G. Maiuri of London has made use of these conclusions and designed and constructed new absorption machines. The results on one of these show refrigeration at −58 deg. F. produced at the rate of 600 B.T.U. per lb. of steam consumed in heating the generator, a performance twice as good as that of the old style machine and three to four times that of a steam driven compression plant. With various fuels the cost of operation is extremely low. Its first cost is lower, it requires less attendance and it requires less space than the compression type. With low temperature refrigeration at such low cost it is natural to look around for fields of application. So far these machines have been employed in liquefaction of CO_2 and storage of it at 120–150. lb. per sq. in pressure, direct freezing of CO_2, quick freezing of perishables in air, quick freezing and hardening of ice cream, and further applications are presenting themselves in rapid succession.

R. H. O.

Design Features of the Lincoln Tunnel.—R. SMILLIE. (*Civil Engineering*, Vol. 7, No. 8.) Another important addition to the vital traffic connections between New Jersey and New York will be inaugurated early in 1938 when the first unit of the Lincoln Tunnel will be opened for public use. It goes under the Hudson River from West 39th St., Manhattan, to Weehawken, N. J. In its final stage it will consist of two separate tubes each providing for two lanes of traffic. The south tunnel, now nearing completion is 8215 ft. long between portals. The pavement is of de-aired vitrified brick set on a ¾ in. mastic cushion. This is a new departure for tunnel pavings. Other new features include the use of glazed terra cotta interior lining for the facing of the bench below the sidewalk and the use of glass tile for ceilings—a new finish.

R. H. O.

Device Measures Surface Reflection.—(*Electrical World*, Vol. 108, No. 3.) A new photometric instrument for determining the light reflecting efficiencies of flat surfaces and light transmission properties of translucent or transparent materials, employs two light-sensitive cells to measure the relative amounts of light received and redirected or transmitted by the sample under test. It is known as the reflectometer and is a development of the General Electric Co. It may be used to measure the reflection factors of all materials provided they have a flat surface and a circular area of 3 in. in diameter.

R. H. O.

Chilowski Light Relay.—(*Successful Inventions*, Vol. II, No. 13.) In view of recent experimental work in connection with electric relays operated by light the apparatus manufactured by Société Tubest, Fere-en-Tardenois, France is of interest. Its action is based on a photo-chemical reaction long known to chemists. If a glass container filled with equal volumes of hydrogen and chlorine gas be exposed to sunlight, the two gases combine instantly. If the light is subdued the rate of combination is slower. In darkness the two gases do not combine. A very small glass bulb is half-filled with aqueous hydrochloric acid and two electrodes are sealed through this container. Electrolysis of the acid takes place, hydrogen and chlorine gases being produced within the glass bulb. If the bulb is in darkness the two do not recombine and a considerable gas pressure is built up in the bulb. One side of this bulb consists of a thin flexible membrane which bends slightly with the increasing gas pressure. The bending motion either operates a direct acting switch or moves a mercury column which closes a circuit. When the glass bulb containing the two gases is exposed to light of a certain intensity the gases recombine, dissolve in the acid, and the pressure is reduced. The membrane returns to normal and the circuit is broken. An important application is the automatic switching on and off of the electric lighting of railway coaches, public lighting systems, display windows, road signs and traffic lights.

R. H. O.

A New Air Cleaner.—G. W. PENNEY. (*The Electric Journal*, Vol. 34, No. 8.) The development of air conditioning has made people more critical of our atmosphere. Because of dust in the air commercial air cleaning devices are far from satisfactory. Dust particles not only consist of numberless substances but also their shape and size vary widely. For instance, ragweed pollen, which is the cause of the common hay fever, consists of particles about 0.0008 inch in diameter. Electrostatic precipitation has long been recognized as the outstanding method of removing fine dust and smoke particles, but it has been suitable only for special applications. Recently a new type precipitator has been developed. It is small and lends itself to manufacture in practical automatic units suitable for air conditioning applications. In this apparatus the air first passes through an ionizing section wherein a small wire is maintained at a direct current potential of about 12,000 volts. This creates an electrostatic stress concentration sufficient to ionize air molecules by collision. All dust particles passing through this ionizing region acquire an electrostatic charge and are attracted toward grounded electrodes. When the particles touch the electrode most of the

electrostatic force disappears so that the particle must be held by adhesion. Most atmospheric dust adheres to a dry electrode but in special cases it is necessary to use a coating to cause adherence. The power input to the precipitator is relatively low. A five cell unit with a capacity of 3750 c.f.m. takes about 85 watts. A 40 cell installation, cleaning about 30,000 c.f.m., requires 500 watts.

R. H. O.

Forecasting Mountain Water Supply by Photographing Snowfall.—D. D. GROSS. (*Engineering News Record*, Vol. 119, No. 8.) It has long been recognized by users of water from streams along the eastern slope of the Rocky Mountains that a bountiful supply of snow along the Continental Divide in April means a bountiful supply of water and vice versa. Demands for accurate information for predictions have resulted in various methods of determination. During the past few years H. L. Potts, water rights engineer for the Denver Board of Water Commissioners, has been developing an original method of forecasting runoff from the accumulated snowfall. At regular times during the year, but most frequently during the past winter and early spring, Mr. Potts has been taking pictures at the same spot on the Continental Divide, located near Hoosier Pass. Each of these pictures is identical as to location and takes in a panorama of many miles, including rugged mountain peaks. After each picture is taken the percentage of the snow area is determined for comparison with other pictures. During the runoff season gaging stations are maintained as a means of checking the amount of water actually produced. Curves are plotted from this information, to which is added a graph to show the amount of precipitation from rain during the late spring and summer. This information is being accumulated with the anticipation that in the future it will be possible, whenever a picture is taken and the percentage of snow area determined, to predict the amount of runoff from snow that can be safely counted upon. Although the photographic investigations have extended over a comparatively short period of time, the results have thus far been gratifying.

R. H. O.